PB-218 048

AIR POLLUTION FROM CHLORINATION PROCESSES

Processes Research, Incorporated

Prepared for:

Environmental Protection Agency

31 March 1972

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PB 218 048

AIR POLLUTION
FROM
CHLORINATION PROCESSES

TASK ORDER NO. 23

CONTRACT NO. CPA 70-1

MARCH 31, 1972

PREPARED FOR

OFFICE OF AIR PROGRAMS
ENVIRONMENTAL PROTECTION AGENCY

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INDUSTRIAL PLANNING AND RESEARCH
CINCINNATI, OHIO

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2.

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16. Abstracts The processes employed for the production of the sixteen most important chlorinated hydrocarbon products were surveyed. Past, present and projected production figures are shown. Chlorination processes are designed to give high efficiency containment of potentially hazardous emissions of Cl_2, HCl, and chlorinated hydrocarbons. Typically, they will have one or more gas cleaning devices installed to collect unreacted gases and vapors so that they can be recycled. The collection methods used are condensation, adsorption, and absorption. Calculated emission factors for processes relying exclusively on condensation control suggest thaty they may not meet the requirements of some agencies, but high levels of control can be effected using sorbent systems so that prevention of air pollution from routine operations does not appear to be dependent upon availability of improved technology. Most of the processes seem unlikely to be prone to run out of control so that it will become necessary to open the reactor to the atmosphere to prevent a disaster. No feedback control system can be designed to respond to Cl_2 and/or HCl in exit gas streams because of the unavailability of methods of analysis for Cl_2 and HCl. The total quantity of air pollutants for each process was calculated for 1970.

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Chemical industry
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Hydrochloric acid
Condensing
Absorption
Adsorption
Exhaust emissions
Chemical analysis

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SECTION I - INTRODUCTION

Industrial use of chlorine is growing at a rapid rate. In 1960, 9.3 billion pounds were used. In 1970, the amount used increased to 19.5 billion pounds and it is estimated that by 1980 we will be producing 45.5 billion pounds for use. About 3.0 percent of the total is used for water sanitation and 16.0 percent is consumed in the pulp and paper industry. The balance of 81.0 percent is used in the production of chlorinated hydrocarbon products. Because of the apparent potential for atmospheric pollution with chlorine, hydrochloric acid and various hydrocarbon compounds, a survey of the processes employed for the production of the sixteen most important chlorinated hydrocarbon products was undertaken. Past, present and projected production figures for these materials are shown in Table I. This list includes all products to which consumption of 1 percent or more of the chlorine used in 1970 could be attributed. Processes producing these sixteen selected products consume 68 percent of the 1970 chlorine production. Table II shows most of the remaining products of commercial importance. The analysis of processes was performed only for those products shown in Table I. It was felt that the twenty processes in this group would be representative of all processes involving chlorine.

Processes and production data were accumulated using forms and techniques developed under Environmental Protection Agency, Office of Air Programs, Contract 70-1, Task Order No. 4. An explanation of the system is shown in Section II of this report.

All of the processes involved in the production of the sixteen major products studied are classifiable as one of five basic process types. A discussion of the process classes is included in Section II.

TABLE 1

MAJOR PRODUCTS FROM CHLORINE

	Required Production of Chlorine		
Product	1960	1970	1980 (Estimated)
	Millions of Pounds/Year		
Carbon tetrachloride, CCl_4	620	1,500	3,420
Chloroform, $HCCl_3$	140	450	1,460
Epichlorohydrin, C_3H_5OCl	300	500	850
Ethyl chloride, C_2H_5Cl	220	300	350
1, 2 - dichloroethane, $C_2H_4Cl_2$	290	2,140	7,070
Allyl chloride, C_3H_5Cl	540	900	1,550
Hydrogen chloride, HCl	380	260	440
Methyl chloride, H_3CCl	130	550	2,000
Methylene chloride, CH_2Cl_2	230	610	1,550
Monochlorobenzene, C_6H_5Cl	420	490	570
Phosgene, $COCl_2$	Nil	400	1,650
Propylene oxide, C_3H_6O	200	820	2,630
Tetrachloroethylene, C_2Cl_4	360	1,340	3,580
1, 1, 1 - trichloroethane, $C_2H_3Cl_3$	Nil	680	2,700
1, 1, 2 - trichloroethylene, C_2HCl_3	470	830	1,820
Vinyl chloride, C_2H_3Cl	450	1,410	4,340
Total	4,750	13,180	35,980
Total chlorine production	9,280	19,500	45,500

TABLE 2

MINOR PRODUCTS FROM CHLORINE

Product	Required Production of Chlorine 1960	1970	1980 (Estimated)
	Millions of Pounds/Year		
Ethylene oxide, C_2H_4O	1,845	-	-
Chloral, C_2Cl_3HO	270	140	80
Dichlorobenzene, $C_6H_4Cl_2$	180	170	240
Benzene hexachloride, C_6Cl_6	70	-	-
Calcium hypochlorite, $Ca(OCl)_2$	30	100	280
Chloroparaffins $(C_{10}-C_{30})Cl$	10	20	60
1, 2 - dichloropropane, $C_3H_6Cl_2$	15	70	210
Monochloroacetic acid, $C_2H_3O_2Cl$	40	80	130
Pentachlorophenol, C_6Cl_5OH	50	60	80
Phosphorus trichloride, PCl_3	-	100	200
Sulfuryl chloride, $SOCl_2$	-	120	160
Vinylidene chloride, $CH_2 = CCl_2$	-	80	-
Minor total	2,510	940	1,440

SECTION II - MANUFACTURING TECHNOLOGY

A. CLASSES OF PROCESSES

The chemical industrial processes involving chlorine can be classified into five groups or types. Starting with the processes which react under the mildest conditions, the classification is as follows:

1. Liquid phase chlorinations at less than 100C and at near atmospheric pressure. In general, these are addition reactions; a typical example being:

$$Cl_2 + C_2H_4 \xrightarrow[\text{7 psig}]{\text{90C}} C_2H_4Cl_2$$

2. Hydrochlorinations at less than 200C and 40 psig. These are addition reactions; a typical example being:

$$HCl + C_2H_4 \xrightarrow[\text{40 psig}]{\text{40C}} C_2H_5Cl$$

3. Vapor phase chlorinations at over 500C and at 2 to 15 psig pressure. In general, these are thermal substitution reactions; a typical example being:

$$2Cl_2 + CH_4 \xrightarrow[\text{15 psig}]{\text{500C}} CH_2Cl_2 + 2HCl$$

4. Vapor phase dehydrochlorinations at over 600C and at less than 60 psig. These are thermal cracking reactions driving off HCl; a typical example being:

$$C_2H_4Cl_2 \xrightarrow[\text{50 psig}]{\text{900C}} CH_2 = CHCl + HCl$$

5. Vapor phase oxychlorination at 300C and 75 psig, namely:

$$C_2H_4 + 2HCl + \underset{\text{(Air)}}{1/2O_2} \xrightarrow[\text{50-100 psig}]{\text{300C}} C_2H_4Cl_2 + H_2O$$

Certain dual step processes have been included in only one classification because the products of this reaction are the only ones on which there are production data. For example, trichloroethylene is made by these two reactions:

$$2Cl_2 + C_2H_2 \longrightarrow C_2H_2Cl_4$$

$$C_2H_2Cl_4 \longrightarrow C_2HCl_3 + HCl$$

The first reaction is a mild addition reaction at 50C and atmospheric pressure, and the second reaction is a thermal dehydrochlorination, carried out at about 600C. There are no production figures for tetrachloroethane, $C_2H_2Cl_4$ (which is very toxic). Therefore, trichloroethylene is discussed under Class 4, Dehydrochlorination.

Other aspects of the classification are the multiple reactions which can be carried out using one raw material. Ethylene can be chlorinated, chlorohydrinated, and hydrochlorinated. Methane has four levels of chlorination: methyl chloride, methylene chloride, chloroform, and carbon tetrachloride.

Table 3 lists the classified processes. The trends in designing plants which use chlorine are to carry out the reactions in the vapor phase under more severe conditions, and to use atmospheric oxygen as a hydrogen stripper. The purpose behind these trends is to provide low capital cost plants with high production capacities. The disadvantages of the trend are higher feed stock consumption due to more side reactions, and more pollutants due to the products of the side reactions.

TABLE 3

CLASSIFICATION OF CHLORINATION/HYDROCHLORINATION PROCESSES

Process Code No.	Process	Product	Number of Vents	1970 Production Millions of Pounds	Reactor Degree C	Conditions Psig	Yields Percent	Reaction Phase	Classification Type
48	Chlorination of propylene	Allyl chloride	3	870	500	15	85	Vapor	3
33	Chlorination of methane	CCl_4	3	0.40 x 900 360	500	15	95	Vapor	3
34	Chlorination of CS_2	CCl_4	2	0.25 x 900 225	85-100	2-4	95	Liquid	1
35	Thermal chlorin. of (C_1 - C_3)	CCl_4	1	0.35 x 900 315	550-700	15	-	Vapor	3
33	Chlorination of methane	$CHCl_3$	3	250	500	15	95	Vapor	3
36	Chlorohydrination then hydrolysis of ally chloride	Epichlorohydrin	2	590	30-80	5	90	Liquid	1
37	Hydrochlorination of C_2H_4	$C_2H_5C_1$	1	.80 x 640 512	35-40	40	90	Liquid	2
38	Chlorination of C_2H_4	$C_2H_4Cl_2$	1	0.85 x 5200 4420	90	7	95	Liquid	1
49	Oxyhydrochlorination of C_2H_4	$C_2H_4Cl_2$	1	0.15 x 5200 780	250-315	50-100	95	Vapor	5
40	Chlorination of H_2	HCl	1	265	600-800	2-4	99	Vapor	3
33	Chlorination of methane	CH_3Cl	3	0.78 x 390 300	500	15	95	Vapor	3
33	Chlorination of methane	CH_2Cl_2	3	330	500	15	95	Vapor	3
50	Chlorination of benzene	C_6H_5Cl	2	600	80-100	2-4	75 LCB 10-20 DCB	Liquid	1
42	Chlorination of carbon monoxide	$COCl_2$	1	560	200	2-4	99	Vapor	3
43	Chlorohydrination then hydrolysis of propylene	C_3H_6O	2	1100	50	2-4	80	Liquid	1
35	Thermal chlorin. of (C_1 - C_3)	C_2Cl_4	1	0.80 x 780 620	550-700	15	-	Vapor	3
44	Hydrochlorination then chlorin. of vinyl chloride	CH_3 - CCl_3	2	420	400 40	2-4 2-4	95	Vapor Liquid	3 2
45	Chlorination then dehydrochlor. of acetylene	$CHCl$ - CCl_2	2	.90 x 590 530	50-80 600	2-4 2-4	-	Liquid Vapor	1 4
47	Dehydrochlorination of $C_2H_4Cl_2$	Vinyl chloride	2	0.80 x 3250 2600	900	50	95	Vapor	4
46	Hydrochlorination of acetylene	Vinyl chloride	1	0.20 x 3250 650	110-200	5-10	85	Vapor	2
39	Chlorination of C_2H_6	C_2H_5Cl	1	0.10 x 640 64	500	15	75	Vapor	3
51	Hydrochlorination of CH_3OH	CH_3Cl	0	0.22 x 390 90	350	2-4	95	Vapor	2
65	Hydrochlorination of C_2H_5OH	C_2H_5Cl	1	0.10 x 640 64	145	30	95-98	Liquid	2
67	Oxychlorination of 1-2 $C_2H_4Cl_2$	C_2HCl_3	1	0.10 x 590 60	300-400	100	90	Vapor	5
66	Chlorination of C_2HCl_3, then dehydrochlorination	C_2Cl_4	1	0.20 x 780 160	80 80	2 2	90	Liquid Liquid	1 -

B. DISCUSSION OF INDUSTRIES, PRODUCTS, PROCESSES, AND SOURCES OF POLLUTION FROM CHLORINATION PROCESSES

Production of the sixteen chlorinated products which have been studied involves the use of twenty different processes. These processes are used in four industries as defined by the Standard Industrial Classification system established by the Department of Commerce. These Department of Commerce industry classifications were used in a recent EPA-OAP funded study aimed at development of a method for cataloging information on all air pollution sources associated with any process used to generate products for which the Department of Commerce routinely collects statistical information. The methodology produced by this earlier study was used to assemble information for the present project. In the earlier study, a system of nomenclature involving the basic categories of "industry," "product," "process," and "source" was developed, using definitions for each category which are believed applicable to all industries. These categories are defined below:

Industry. An industry, as defined for cataloging purposes, will correspond with headings in the SIC Manual. This manual is subdivided into "Major Group," each with a unique two-digit numerical code, and subcategories within each Major Group called "Group Number," each of which has a number of designated subgroups called "Industry Number." For example, Major Group 28 "Chemicals and Allied Products" includes the Group Number 281 "Industrial Inorganic and Organic Chemicals," which is further subdivided into Industry Number groups such as 2818 - "Industrial Organic Chemicals Not Elsewhere Classified" and 2819 - "Industrial Inorganic Chemicals Not Elsewhere Classified." Under each four-digit industry number, a listing of included products is shown. Two-digit major group titles, three-digit group number titles, or four-digit industry number titles were selected for use with this system, depending on anticipated importance of the category as far as air pollution is concerned. Where initial selection of two-digit or three-digit categories leads to an excessive number of processes in a given category, the original group can be divided subsequently into the smaller three-digit or four-digit subgroups.

Process. As the term is used here, it includes both processes in which a single product is prepared by a specific procedure involving chemical change or change in state, and unit operations where a class of products is manufactured by use of essentially identical equipment and operations, e.g., the product sulfuric acid is produced both by the chamber process and by the contact process, and both would be included as processes. Also included in the classification of process would be the unit operations such as galvanizing, degreasing, and other unit operations used in the manufacture of many different fabricated metal products. All such processes fall within some industry category as previously defined. Where there is doubt as to which industry category is appropriate, the classification is determined by locating the category in which the product of the process is listed in the index for the SIC Manual.

Product. As the term is used for this study, it includes all products listed in the SIC Manual. This category is useful for relating process to industry as described in the SIC codes. Also, it is useful as a subdivision for certain industries such as 2818 - Industrial Organic Chemicals, where a large number of processes are included, despite the fact that the smallest subdivision in the SIC Manual is used for definition of the industry. For complex industries, the product category would be used. For less complex industries, only the basic terms industry, process, and source would be used.

Source. As defined for the study, a source is a piece of equipment, essential to the economic operation of a process, from which air pollution emissions occur unless the emissions are prevented by application of pollution control technology. By contrast, a piece of equipment installed for the primary purpose of minimizing air pollution emissions is considered control equipment for a source. Thus a specific type of equipment, such as a scrubber, may be classifiable as a source or as control equipment, depending on its role in the process.

The general format developed for cataloging information on all industries, products, processes and sources, is illustrated by the following description of chlorination processes. Abbreviations and mechanics of this system are also defined below:

1. Product. For each product, a general discussion on how the product is made from various processes is included, along with production and capacity data from 1960. Also included is a 1980 production forecast and the principal uses of the product.

2. Process. For each specific process, a detailed description has been included, along with a process flow sheet, covering these items: feed preparation, reaction conditions, product purification, recycle systems, raw materials, by-products and sources of air pollution.

3. Process Data Tabulation. This sheet tabulates the producers, the location of their plants along with the Air Quality Control Regions (AQCR), the capacity of the plants in millions of pounds per year and rates the quality of the data. See attached form.

4. Source Data Tabulation. This sheet tabulates the sources or origins of air pollution. It defines the composition of the pollutant and the quantity of emissions in pounds per ton of product. It shows the effect of control devices and the extent that control devices are used.

5. Data Limitations. Complete and valid data were not always available. Therefore, it became necessary in some instances to estimate emission factors, source control factors, processes, or production levels. To qualify the validity of the data, the following code was used:

A = Valid data. The result of census or experiment.

B = Estimated data. Estimate based on limited census or experimental data.

C = Estimated data. Estimate based on little or no census or experimental data.

Emission factors which were used were an average factor for all sources, and the source factor (estimated percent of existing sources which are controlled) is a national average. Application of such numbers to individual plants or to a small number of plants in a given geographical area could yield erroneous results.

PROCESS DATA TABULATION

SH____ OF ____

SIC. NO.	INDUSTRY	PRODUCT
DATE:	PROCESS	

COMPUTER CODE NOS.

SIC. NO. :	COLS. 1-4	☒					
PRODUCT :	COLS. 5-8	☒					
PROCESS :	COLS. 9-13						

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 49	☒ 50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
DATE PREPARED	PROCESS	SOURCE	

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒					
PRODUCT : COLS. 5-8	☒					
PROCESS : COLS. 9-13						
SOURCE : COLS. 14-17	☒					

POLLUTANT | CONTROL DEVICE

DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23	UNCON EMISS 24 30	Q 31	CEF 32 35	Q 36	SCF 37 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE	

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ______________________

RELATED INDUSTRIES

BIBLIOGRAPHY

C. CATALOG OF SOURCES FROM CHLORINATION PROCESSES

1. Cyclic Intermediates - SIC Industry No. 2815

Establishments primarily engaged in manufacturing cyclic organic intermediates. Important products of this industry include:

Derivatives of benzene, toluene, naphthalene, anthracene, pyridine, carbazole, and other cyclic chemical products
Synthetic dyes
Synthetic organic pigments
Cyclic (coal tar) crudes

Some of the chlorinated products of this industry include:

Benzene hexachloride
Monochlorobenzene
Chloronaphthalene
Chlorophenol
Chlorotoluene
Pentachlorophenol

Only monochlorobenzene has enough production to be included in this study. In general, this industry (No. 2815) is not a big consumer of chlorine or chlorinated products.

Product: Monochlorobenzene

Where the end product is monochlorobenzene, benzene is chlorinated in the liquid phase reaction:

$$C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl$$

As an intermediate for phenol, these oxychlorination reactions are used:

$$C_6H_6 + HCl + 1/2\ O_2 \longrightarrow C_6H_5Cl + H_2O$$

$$C_6H_5Cl + H_2O \longrightarrow C_6H_5OH + HCl$$

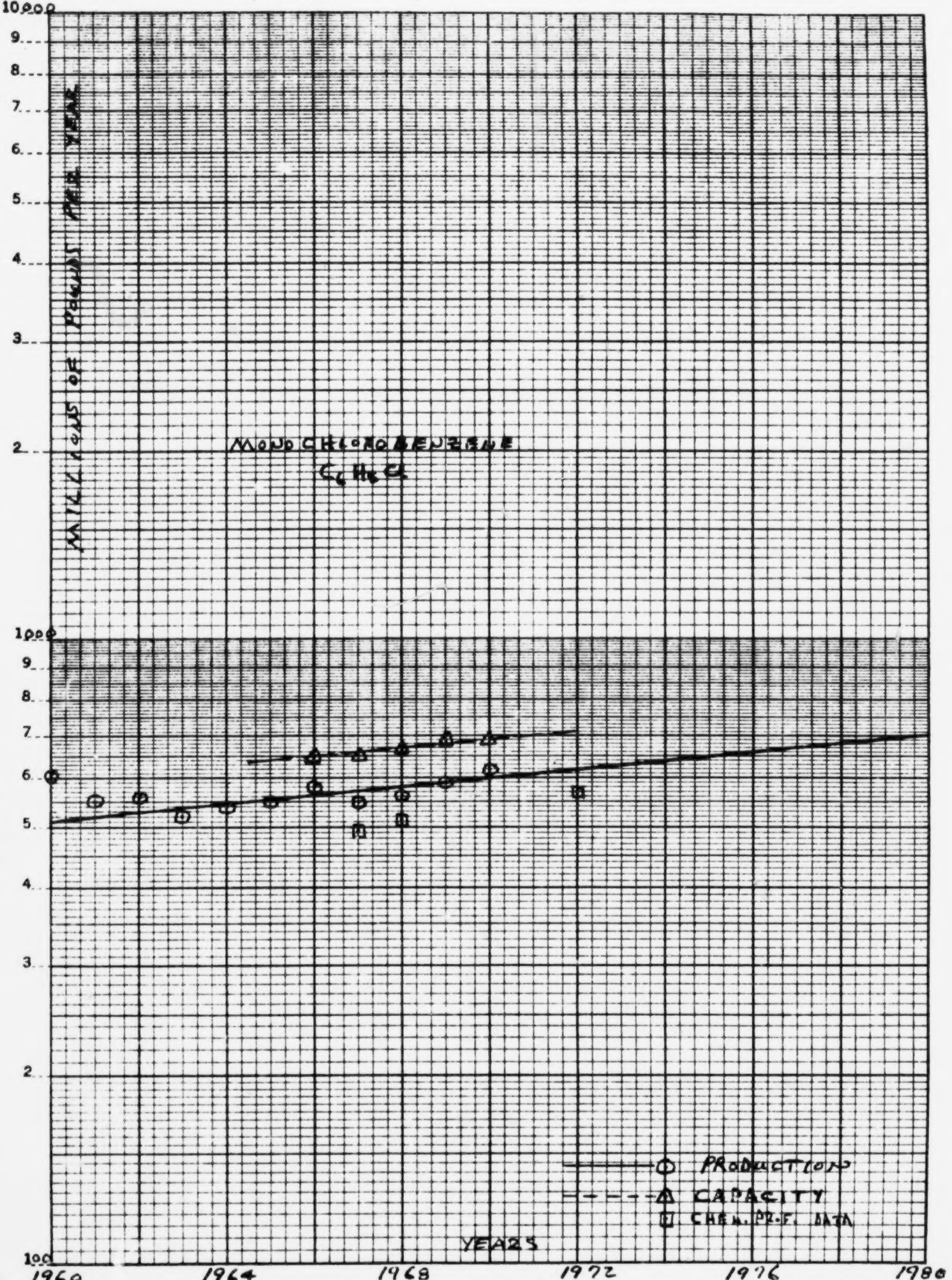
without the separation of the monochlorobenzene. The volume of the oxychlorination reaction is about twice that of the direct chlorination process. However, phenol production is outside the scope of this study.

The production and capacities of monochlorobenzene, from 1960 through 1970, have been plotted on Chart 4. A projection indicates that, in 1980, the production will be approximately 700 million pounds. With the decline of DDT production, it is expected that the growth rate of monochlorobenzene will be small.

The raw materials are benzene, chlorine, iron turnings, and sodium hydroxide. The by-products are hydrogen chloride, dichlorobenzenes, heavies and spent caustic sludge.

The main use of monochlorobenzene is as an intermediate, for example, DDT or nitrochlorobenzene.

CHART 4


10,000
9
8
7
6
5
4
3
2
1000
9
8
7
6
5
4
3
2
100
MILLIONS OF POUNDS PER YEAR
MONOCHLOROBENZENE
C_6H_5Cl
PRODUCTION
CAPACITY
CHEM. PR.F. DATA
YEARS
1960
1964
1968
1972
1976
1980
KEUFFEL & ESSER CO.

Process: Chlorination of Benzene

Benzene and chlorine are fed to a liquid phase reactor containing iron turnings as a catalyst. The liquid phase is a boiling mixture of chlorobenzenes and benzene. The pressure is atmospheric and the temperature range is 80 to 100C. The HCl from the reaction is scrubbed with recycled benzene for hydrocarbon removal and then absorbed in water forming 20°Be hydrochloric acid.

The bottoms from the reactor are washed with sodium hydroxide to remove the last of the HCl and most of the dichlorobenzenes. After decanting from the sodium hydroxide solution, the product is fed to a stripping column, where the benzene is stripped off overhead and the benzene is recycled to the HCl scrubber. The bottoms from the stripper are fed to a fractionating column where the pure monochlorobenzene is taken off overhead and where the bottoms are mostly dichlorobenzenes. Yields of monochlorobenzene are about 75 percent, while dichlorobenzene yields are 10 to 20 percent.

There are two sources of air pollution, the vent on the tail gas absorber and the vent on the stripper. The vents are continuous. Benzene is the major air pollutant.

FLOWSHEET

Job EPA

Location CHLORINE STUDY

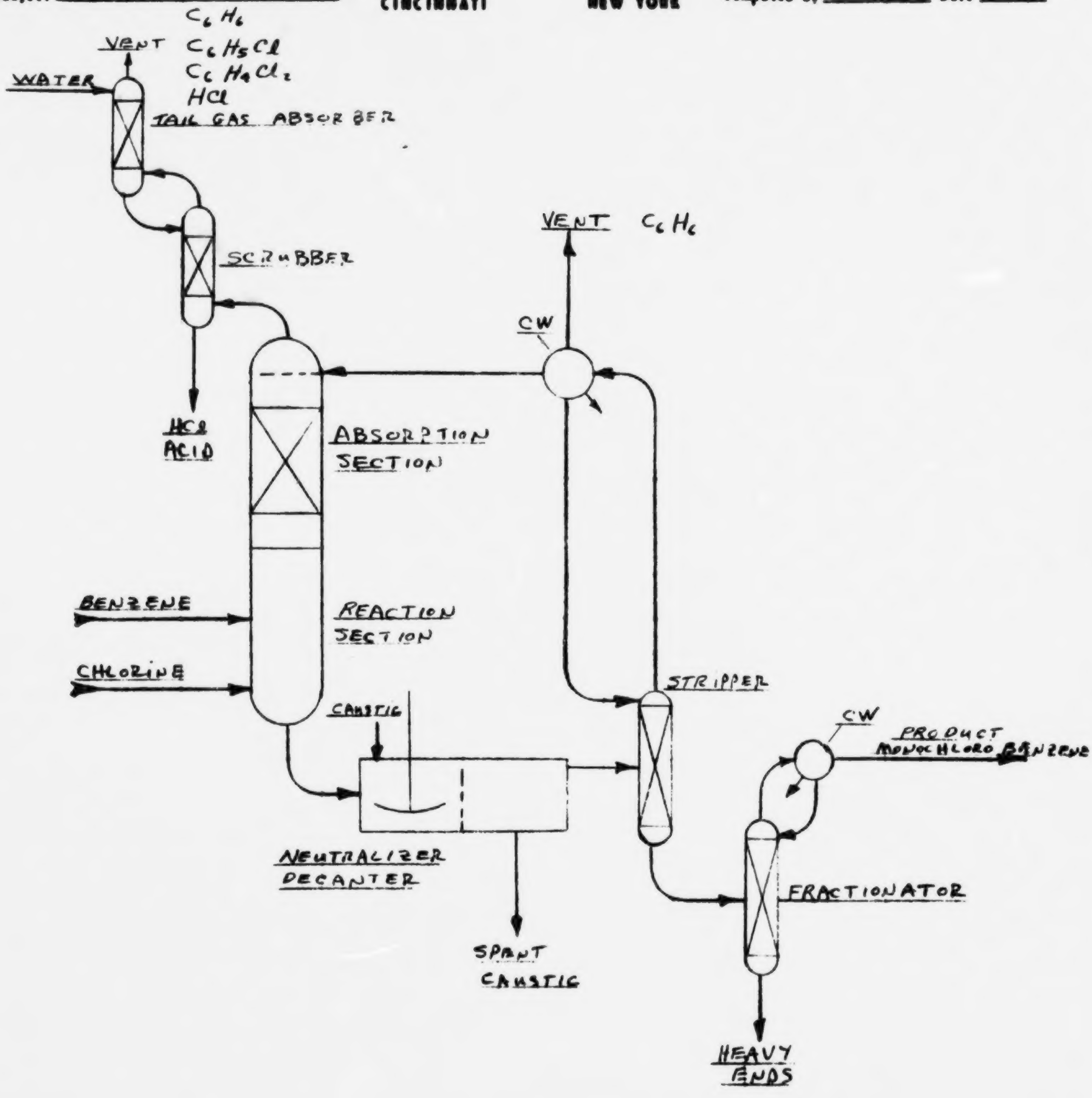
Subject MONOCHLORO BENZENE

PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING AND RESEARCH
CINCINNATI NEW YORK

File No. 03383 Sheet No. 1

Checked by ______ Date ______

Computed by SPK Date 11-3-71



C_6H_6
VENT
C_6H_5Cl
$C_6H_4Cl_2$
HCl
WATER
TAIL GAS ABSORBER
SCRUBBER
HCl ACID
VENT C_6H_6
CW
ABSORPTION SECTION
BENZENE
REACTION SECTION
CHLORINE
CAUSTIC
STRIPPER
CW
PRODUCT MONOCHLORO BENZENE
NEUTRALIZER DECANTER
FRACTIONATOR
SPENT CAUSTIC
HEAVY ENDS

PROCESS: CHLORINATION OF BENZENE

PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO. 2815	INDUSTRY CYCLIC INTERMEDIATE	PRODUCT MONOCHLORO- BENZENE, C_6H_5Cl
DATE: 10-16-72	PROCESS CHLORINATION OF BENZENE	

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒	2	8	1	5	
PRODUCT : COLS. 5-8	☒		1	2	5	
PROCESS : COLS. 9-13				5	0	

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
127	ALLIED	SYRACUSE, N.Y.	A	25	A
205	DOVER	DOVER, OH	A	1	A
195	DOW	MIDLAND, MI	A	350	A
24	HOOKER	NIAGARA FALLS, N.Y.	A	15	A
18	MONSANTO	SAUGET, IL	B	100	A
4166	MONTROSE	HENDERSON, NV	A	70	A
266	OLIN	McINTOSH, AL	B	30	A
70	PPG	NEW MARTINSVILLE, WV	A	50	A
15	STANDARDCHLORO	DELAWARE CITY, DE	A	50	A
15	DuPONT	DEEPWATER, NJ	A	10	B
266	GEIGY	McINTOSH, AL	B	20	B

COMPUTER CODE NOS.

AQCR 19-22	STATE 23 24	CITY 25-36	COMPANY 37-49	☒ 50 51	CAPACITY 52-55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

1/2

INDUSTRY NO. 2815	**INDUSTRY** CYCLIC INTERMEDIATE	**PRODUCT** MONOCHLOROBENZENE C_6H_5Cl	
DATE PREPARED 10-26-71	**PROCESS** CHLORINATION OF BENZENE	**SOURCE** TAIL GAS ABSORBER	

COMPUTER CODE NOS.

SIC. NO. :	COLS. 1-4	☒	2	8	1	5
PRODUCT :	COLS. 5-8	☒		1	2	5
PROCESS :	COLS. 9-13				5	0
SOURCE :	COLS. 14-17	☒			4	1

POLLUTANT			CONTROL DEVICE				
DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
C_6H_6	7.4	C	NONE				
C_6H_5Cl	1.3	C	NONE				
HCl	0.001	C	NONE				
$C_6H_4Cl_2$	0.1	C	NONE				

COMPUTER CODE NOS.

PNO 18-20	CNO 21-23	UNCON EMISS 24-30	Q 31	CEF 32-35	Q 36	SCF 37-40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ______

RELATED INDUSTRIES

BIBLIOGRAPHY

SOURCE DATA TABULATION

2/2

INDUSTRY NO. 2815	**INDUSTRY** CYCLIC INTERMEDIATE	**PRODUCT** MONOCHLOROBENZENE C_6H_5Cl	
DATE PREPARED 10-26-71	**PROCESS** CHLORINATION OF BENZENE	**SOURCE** STRIPPER	

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒	2	8	1	5
PRODUCT : COLS. 5-8	☒		1	2	5
PROCESS : COLS. 9-13				5	0
SOURCE : COLS. 14-17	☒			3	6

POLLUTANT			CONTROL DEVICE				
DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
C_6H_6	15.2	C	NONE				

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23	UNCON EMISS 24 30	Q 31	CEF 32 35	Q 36	SCF 37 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE	

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING

RELATED INDUSTRIES

BIBLIOGRAPHY

2. Industrial Organic Chemicals Not Elsewhere Classified - SIC Industry No. 2818

Establishments primarily engaged in manufacturing industrial organic chemicals, not elsewhere classified. Important products of this industry include:

- Non-cyclic organic chemicals
- Solvents such as alcohols, acetates, ethers, ketones, and chlorinated hydrocarbons
- Polyhydric alcohols
- Synthetic perfume and flavoring materials
- Rubber processing chemicals
- Plasticizers
- Synthetic tanning agents
- Chemical warfare gases
- Esters and amines of polyhydric alcohols

Some of the chlorinated products of this industry include:

- Bromochloromethane
- Carbon tetrachloride
- Chloral
- Chlorinated solvents
- Chloroacetic acid
- Chloroform
- Chloropicrin
- Dichlorodifluoromethane
- Ethyl chloride
- Methyl chloride
- Methylene chloride
- Monochlorodifluorormethane
- Perchloroethylene
- Phosgene
- Tetrachloroethylene
- Trichloroethylene

Thirteen products from this industry have been included in the study. This industry (No. 2818) is a major consumer of chlorine and chlorinated products and is the principal source of air pollutants from the chlorination processes.

Product: 1,2-Dichloroethane

In 1970 approximately 85 percent of the 1,2-dichloroethane (DCE) was made by chlorinating ethylene in the liquid phase, namely:

$$Cl_2 + C_2H_4 \longrightarrow C_2H_4Cl_2$$

The remaining portion of DCE is made by a newer process, the oxychlorination of ethylene, namely:

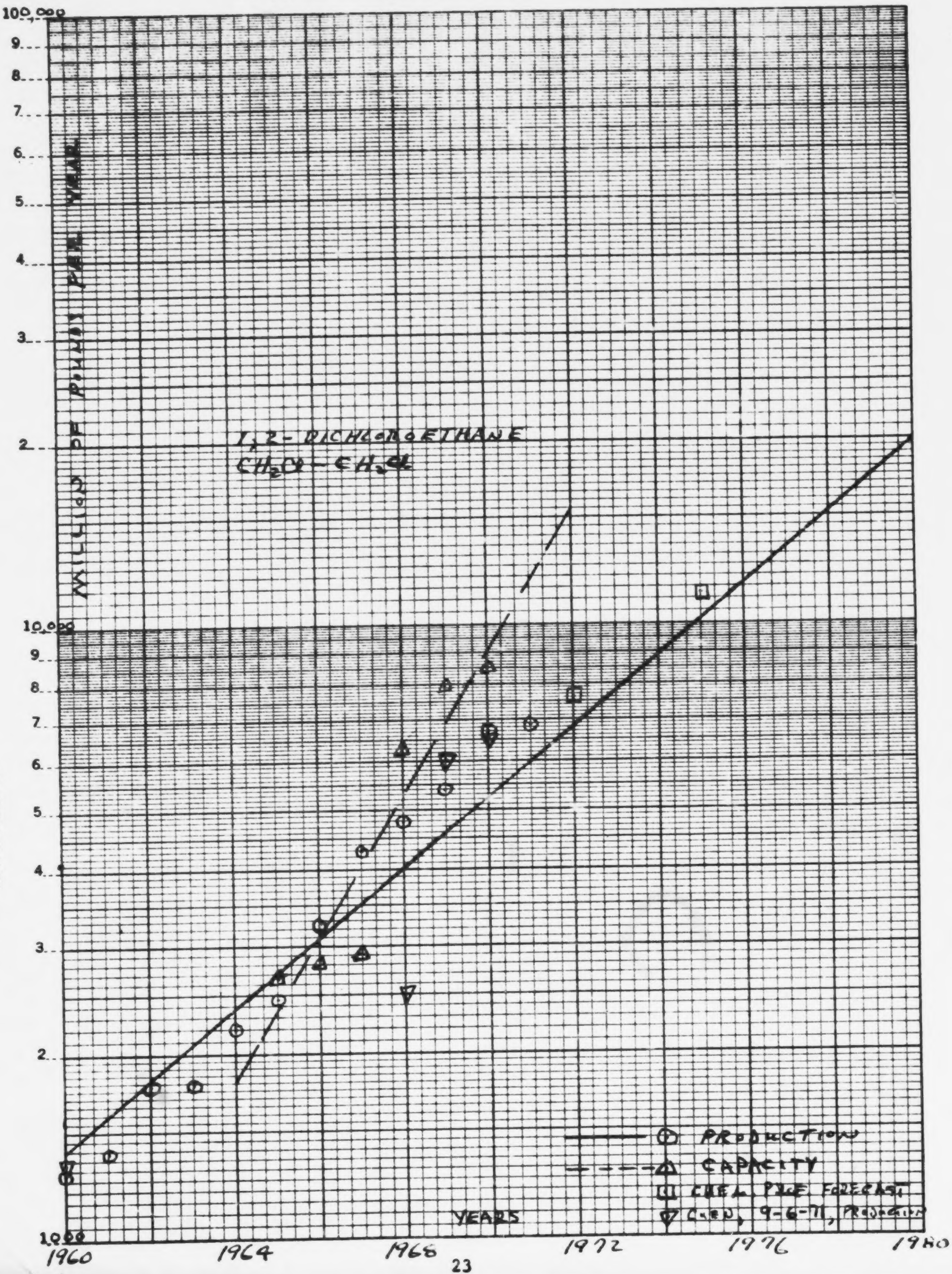
$$2\ HCl + 1/2\ O_2\ (Air) + C_2H_4 \longrightarrow C_2H_4Cl_2 + H_2O$$

Because of cheaper raw materials and good yields (95 percent), most new facilities are using the oxychlorination process.

DCE is the largest product of the chlorohydrocarbon compounds. It is used as an intermedia for vinyl chloride, chlorinated solvents and antiknock compounds. It is expected that 1,2-dichloroethane will have a 10 to 12 percent annual growth rate.

Chart 3 shows a plot of total 1,2-dichloroethane production from 1960 to 1970 along with capacity data.

CHART 3



E 31 YEAR C 485
2 CYCLES X 60 DIVISIONS MADE IN U.S.A.
KEUFFEL & ESSER CO.

Process: Ethylene Chlorination

Chlorine gas and ethylene gas are fed into the bottom of a tower-type reactor filled with liquid DCE, containing some ferric chloride catalyst. The temperature is about 90C and the pressure about 7 pounds per square inch gage. The reaction at these conditions is fast, complete, and exothermic, with some formation of 1,1,2-trichloroethane. The top of the reactor vessel is a fractionator, complete with reflux condenser. Liquid 1,2-dichloroethane, which is 99 percent pure, is withdrawn from near the top of the fractionator. Yields are about 95 percent.

The raw materials are ethylene, acetylene-free chlorine, and ferric chloride catalyst. The by-products are 1,1,2-trichloroethane and hydrogen chloride.

The vent on the reflux condenser, which runs continuously, is the only source of air pollutants.

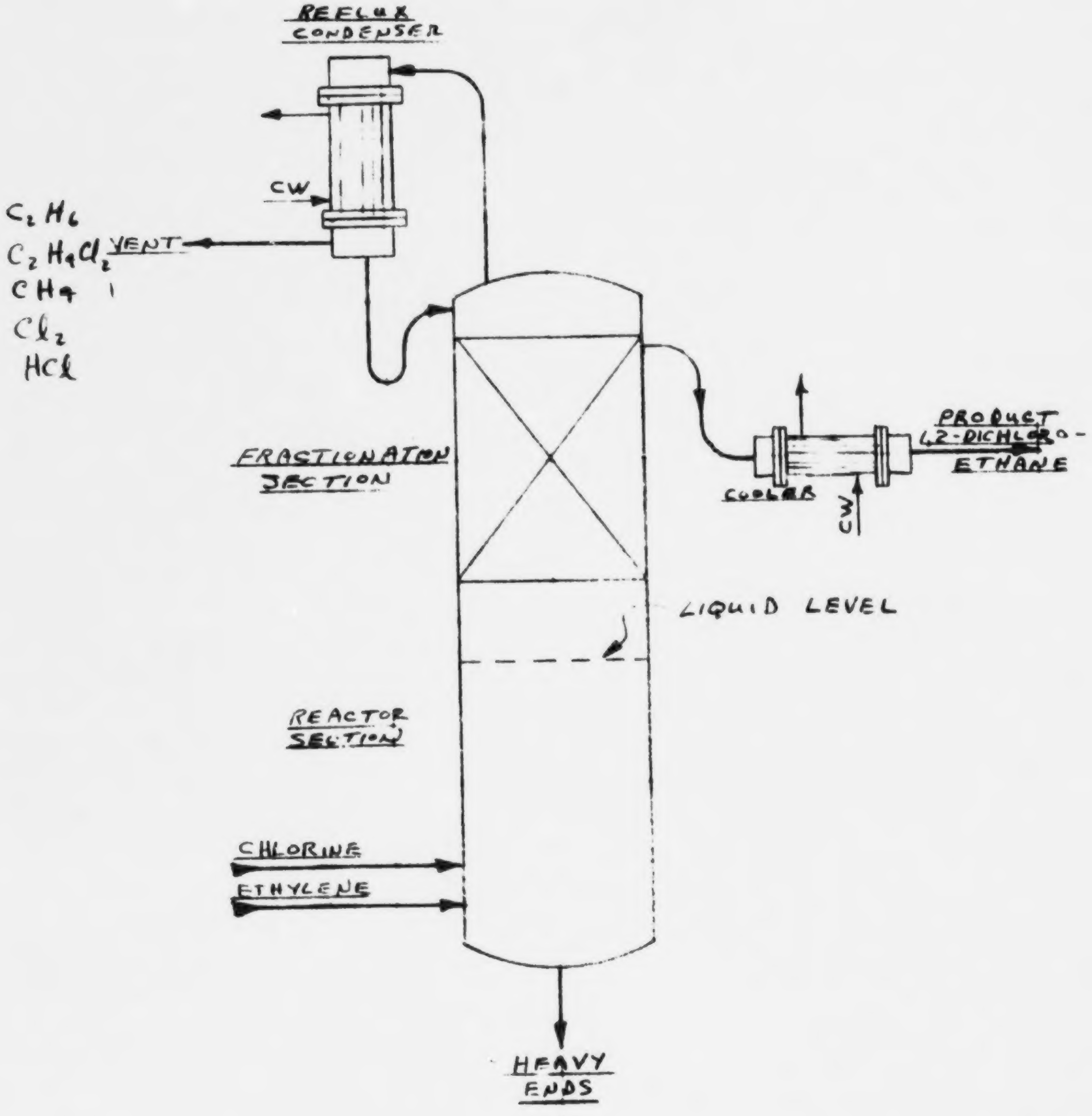
FLOWSHEET

PR 109

PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING
AND RESEARCH
CINCINNATI NEW YORK

Job EPA
Location CHLORINE STUDY
Subject 1,2- DICHLORO ETHANE

File No 3383 Sheet No 1
Checked by ______ Date ______
Computed by SPK Date 11-3-71


REFLUX CONDENSER
CW
C_2H_6
$C_2H_4Cl_2$
CH_4
Cl_2
HCl
VENT
FRACTIONATION SECTION
PRODUCT 1,2-DICHLORO-ETHANE
COOLER
CW
LIQUID LEVEL
REACTOR SECTION
CHLORINE
ETHYLENE
HEAVY ENDS

PROCESS: CHLORINATION OF ETHYLENE

PROCESS DATA TABULATION

SH____OF_____

SIC. NO. 2818	**INDUSTRY** IOC	**PRODUCT** 1,2-DICHLOROETHANE $C_2H_4Cl_2$
DATE: 2-22-72	**PROCESS** CHLORINATION OF ETHYLENE	

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒	2	8	1	8	
PRODUCT : COLS. 5-8	☒		1	2	0	
PROCESS : COLS. 9-13					3	6

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
17	AMERCHEM	LONG BEACH, CA.	A	325	A
53	CONOCO	LAKE CHARLES, LA	A	1000	A
38	DOW	OYSTER CREEK, TX	A	2100	A
53	DOW	PLACQUEMINE, LA	A	1160	A
53	ETHYL	BATON ROUGE, LA	A	500	A
53	PPG	LAKE CHARLES, LA	A	850	A
38	UNION CARBIDE	TEXAS CITY, TX	A	150	A
53	VULCAN	GEISMAR, LA	A	240	A
38	ETHYL	HOUSTON, TX	A	250	A

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 49	☒ 50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO. 2818	**INDUSTRY** IOC	**PRODUCT** 1,2 - DICHLOROETHANE $C_2H_4Cl_2$	**COMPUTER CODE NOS.**
DATE PREPARED 10-26-71	**PROCESS** CHLORINATION OF ETHYLENE	**SOURCE** REFLUX CONDENSER	

COMPUTER CODE NOS.						
SIC. NO.	COLS. 1-4	☒	2	8	1	8
PRODUCT	COLS. 5-8	☒		1	2	0
PROCESS	COLS. 9-13				3	8
SOURCE	COLS. 14-17	☒			4	2

POLLUTANT / CONTROL DEVICE

DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
C_2H_6	6	C	NONE				
$C_2H_4Cl_2$	15	C	"				
CH_4	6	C	"				
Cl_2	0.001	C	"				
HCl	0.001	C	"				

COMPUTER CODE NOS.

PNO 18-20	CNO 21-23	UNCON EMISS 24-30	Q 31	CEF 32-35	Q 36	SCF 37-40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ____________

RELATED INDUSTRIES

BIBLIOGRAPHY

Process: Oxychlorination of Ethylene

Pure ethylene, hydrogen chloride, and air are reacted in the vapor phase over a fixed bed catalyst of cupric chloride on alumina. Conditions are 250 to 315C and 50-100 pounds per square inch gage. The reaction is fast and exothermic. The resulting reaction products are passed through a caustic scrubbing tower where the DCE is condensed, the excess hydrogen chloride is absorbed and neutralized, and the inerts and noncondensable gases are vented. The bottoms from the caustic scrubbing tower are passed to a decanter tank, where the bottom layer is the crude product, DCE. The decanter bottoms are fractionated to yield a 99 percent pure product. The yields are over 95 percent.

The raw materials are ethylene, hydrogen chloride, air, caustic soda, and cupric chloride catalyst. The by-products are carbon dioxide, 1,1,2-trichloroethane, 1,2-dichloroethylene, water, and spent caustic soda.

There is one source of air pollution, the vent from the caustic scrubbing tower.

PR 109

FLOWSHEET

Job EPA

Location CHLORINE STUDY

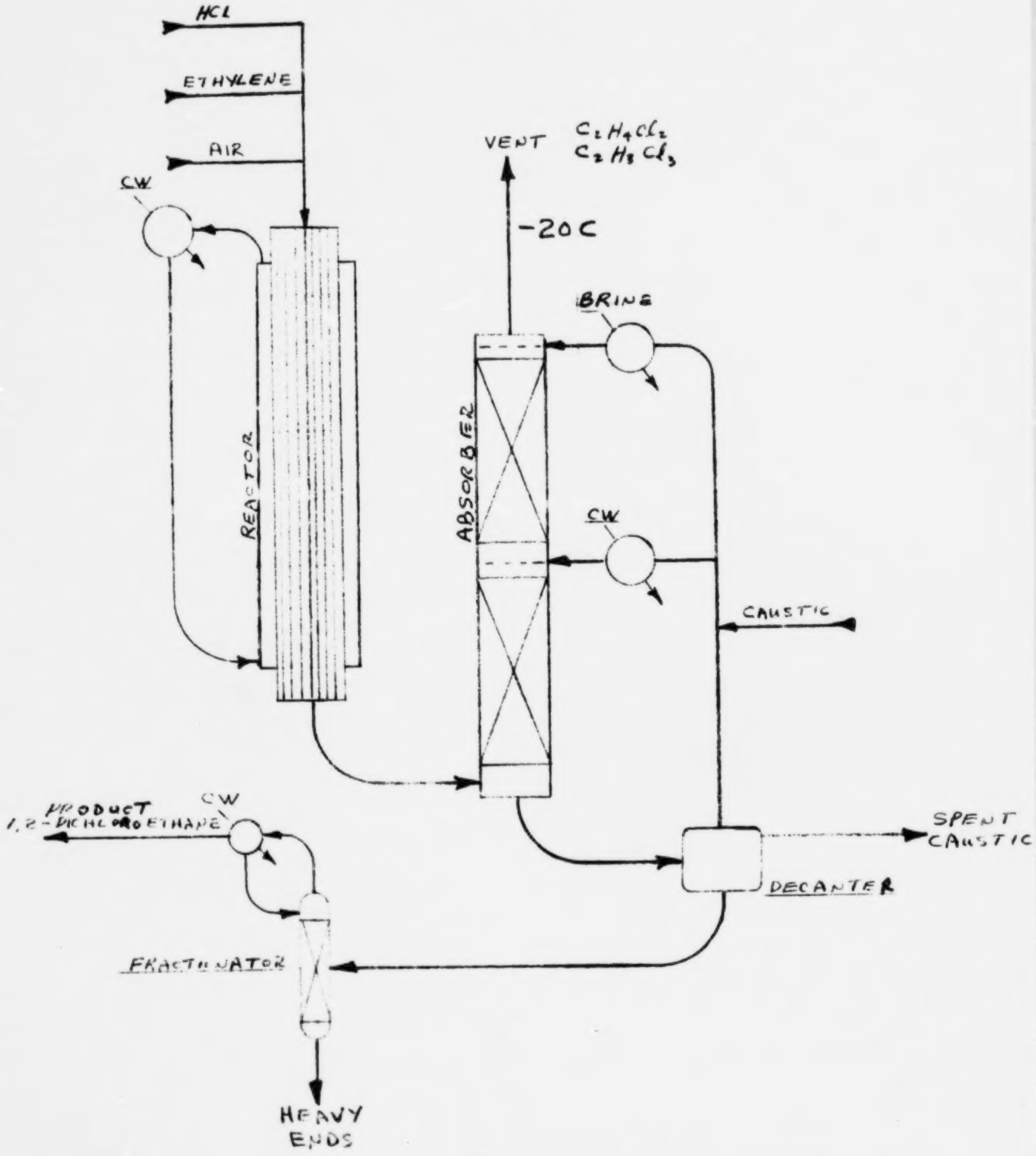
Subject 1,2-DICHLOROETHANE

PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING AND RESEARCH
CINCINNATI NEW YORK

File No. 03383 Sheet No 1

Checked by ______ Date ______

Computed by SPK Date 11-3-71


HCL
ETHYLENE
AIR
CW
REACTOR
VENT $C_2H_4Cl_2$ $C_2H_3Cl_3$
-20C
BRINE
ABSORBER
CW
CAUSTIC
SPENT CAUSTIC
DECANTER
PRODUCT 1,2-DICHLOROETHANE
CW
FRACTIONATOR
HEAVY ENDS

PROCESS: OXYCHLORINATION OF ETHYLENE

PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO.	INDUSTRY	PRODUCT
2818	IOC	1,2- DICHLORO-ETHANE

DATE:	PROCESS
11-1-71	OXYCHLORINATION OF ETHYLENE

COMPUTER CODE NOS.

SIC. NO. :	COLS. 1-4	☒	2	8	1	8
PRODUCT :	COLS. 5-8	☒		1	2	0
PROCESS :	COLS. 9-13				4	9

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
53	ALLIED	BATON ROUGE, LA	A	500	A
69	GOODRICH	CALVERT CITY KY	A	800	A
38	DIAMOND	DEER PARK, TX	A	110	A
53	UNION CARBIDE	TAFT, LA	A	150	A

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 49	50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO. 2818	**INDUSTRY** IOC	**PRODUCT** 1,2-DICHLORO-ETHANE	
DATE PREPARED 11-1-71	**PROCESS** OXYCHLORINATION OF ETHYLENE	**SOURCE** ABSORBER	

COMPUTER CODE NOS.

SIC. NO. :	COLS. 1-4	☒	2	8	1	8
PRODUCT :	COLS. 5-8	☒		1	2	0
PROCESS :	COLS. 9-13				4	9
SOURCE :	COLS. 14-17	☒				1

POLLUTANT / CONTROL DEVICE

DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
1,1 $C_2H_4Cl_2$	40	C	NONE				
1,2 $C_2H_4Cl_2$	51	C	"				
1,1,2 $C_2H_3Cl_3$	15	C	"				

COMPUTER CODE NOS.

PNC 18 20	CNO 21 23	UNCON EMISS 24 30	Q 31	CEF 32 35	Q 36	SCF 37 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ______

RELATED INDUSTRIES

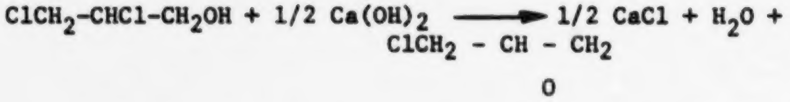
BIBLIOGRAPHY

Product: Epichlorohydrin

Epichlorohydrin was initially developed as an intermediate for synthetic glycerol, but more recently has become an epoxy resin component. Using a two-step process, it is made by chlorohydrinating allyl chloride:

$$ClCH_2\text{-}CH = CH_2 + HOCl \longrightarrow ClCH_2\text{-}CHCl\text{-}CH_2OH$$

followed by hydrolysis to epichlorohydrin:



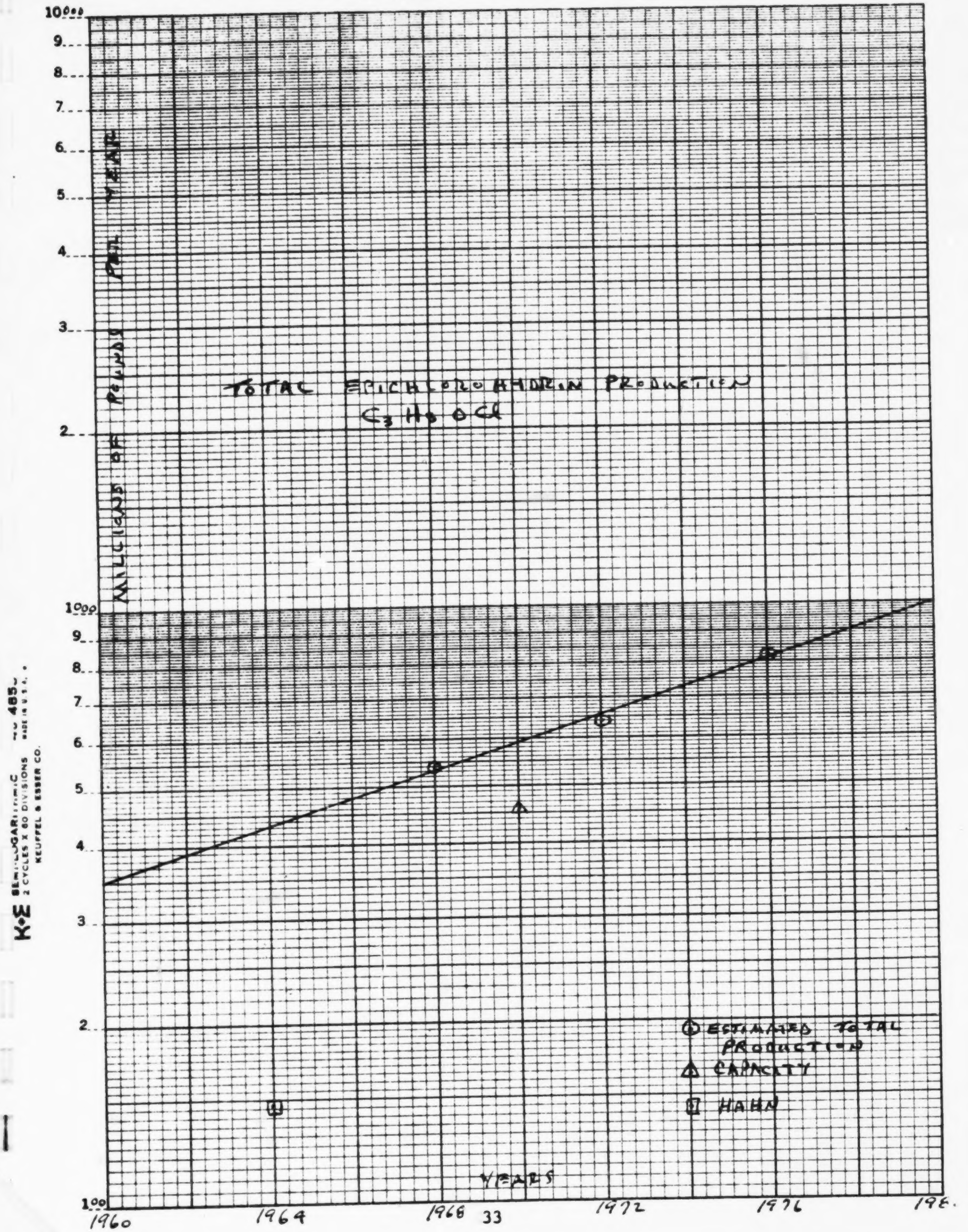
$$ClCH_2\text{-}CHCl\text{-}CH_2OH + 1/2\ Ca(OH)_2 \longrightarrow 1/2\ CaCl + H_2O + ClCH_2 - \underset{O}{CH - CH_2}$$

Chart 2 shows an estimate of total epichlorohydrin production.

Epichlorohydrin is a new compound but is expected to have good growth due to the needs for epoxy resins and glycerol.

Although the hydrolysis reaction second step is not a chlorination process, in general the hydrolysis step immediately follows the chlorohydrination, and production figures are not available on the intermediate.

CHART 2


TOTAL EPICHLOROHYDRIN PRODUCTION
C_3H_5OCl
MILLIONS OF POUNDS PER YEAR
10000
9
8
7
6
5
4
3
2
1000
9
8
7
6
5
4
3
2
100
YEARS
1960
1964
1968
1972
1976
198.
ESTIMATED TOTAL PRODUCTION
CAPACITY
HAHN
K·E SEMI-LOGARITHMIC 2 CYCLES X 60 DIVISIONS
KEUFFEL & ESSER CO.
46 4850 MADE IN U.S.A.

Process: Chlorohydrination of Allyl Chloride

The first reaction, the chlorohydrination of allyl chloride, can be carried out in a stirred tank at atmospheric pressure in the liquid phase, using water as the solvent. The temperature range is 30 to 80C, with some heat evolution. Yields are over 90 percent. The reaction is complete when no more chlorine can be added.

The raw materials of the first step are allyl chloride, chlorine, and water. The by-products are trichloropropane, tetrachloropropyl ether and hydrogen chloride.

Most of the air pollutants, such as HCl, are absorbed in the tail gas absorber.

Reactor products from the chlorohydrination of allyl chloride are treated with a lime slurry in a column-type reactor, using trichloropropane as a solvent. The temperature range is 70 to 100C with some heat evolution. Atmospheric pressure is used. In a crude stripping column most of the water and trichloropropane are distilled off and recycled to the liming column. The bottoms from the crude column are fed to the product distillation column, where the epichlorohydrin is withdrawn overhead. The bottoms of the product column are extracted with water, the water extraction being fed back to the reactor. The solids are settled out of the washed bottoms, and the liquor is returned to the solvent tank.

The raw materials of the second step are dichlorohydrin and calcium hydroxide, while the by-products are calcium chloride and water. The reactor column is vented.

FR 109

FLOWSHEET

Job EPA

Location CHLORINE STUDY

Subject EPICHLOROHYDRIN

PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING
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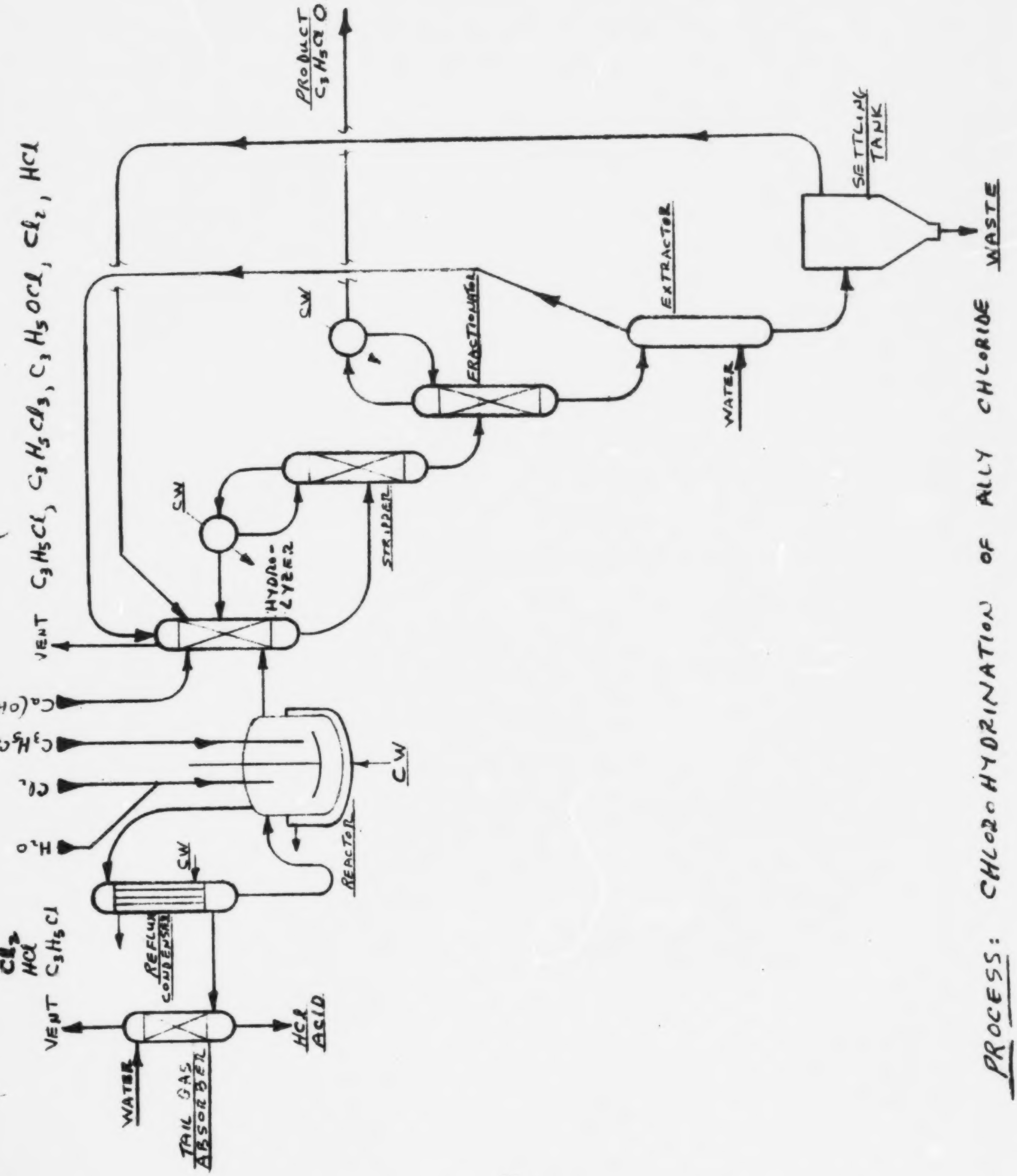
CINCINNATI NEW YORK

File No. 3383 Sheet No 1

Checked by ______ Date ______

Computed by SPK Date 11-3-71


VENT
Cl_2
HCl
C_3H_5Cl
WATER
TAIL GAS ABSORBER
HCl ACID
REFLUX CONDENSER
SW
H_2O
Cl_2
C_3H_5Cl
$Ca(OH)_2$
REACTOR
CW
VENT
C_3H_5Cl, $C_3H_5Cl_3$, C_3H_5OCl, Cl_2, HCl
HYDRO-LYZER
SW
STRIPPER
CW
FRACTIONATOR
EXTRACTOR
WATER
SETTLING TANK
WASTE
PRODUCT C_3H_5ClO

PROCESS: CHLOROHYDRINATION OF ALLY CHLORIDE

PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO. 2818	INDUSTRY IOC	PRODUCT EPICHLOROHYDRIN C_3H_6OCl
DATE: 10-26-71	PROCESS CHLOROHYDRINATION OF ALLYL CHLORIDE	

COMPUTER CODE NOS.

SIC. NO. :	COLS. 1-4	☒	2	8	1	8	
PRODUCT :	COLS. 5-8	☒		1	1	9	
PROCESS :	COLS. 9-13				3	6	

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
UNCL	CIBA	TOMS RIVER, NJ	A	35	A
38	DOW	FREEPORT, TX	A	200	A
38	SHELL	DEER PARK, TX	A	220	A
22	GOODRICH	AVON LAKE, OH	A	8	B
233	UNION CARBIDE	SO. CHARLESTON WV	A	20	A

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 49	50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO. 2818	**INDUSTRY** IOC	**PRODUCT** EPICHLOROHYDRIN C_3H_5OCl	**COMPUTER CODE NOS.**
DATE PREPARED 10-26-71	**PROCESS** CHLOROHYDRINATION OF ALLY CHLORIDE	**SOURCE** TAIL GAS ABSORBER	

SIC. NO. : COLS. 1-4	☒	2	8	1	8
PRODUCT : COLS. 5-8	☒		1	1	8
PROCESS : COLS. 9-13				3	6
SOURCE : COLS. 14-17	☒			4	1

POLLUTANT / CONTROL DEVICE

DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
Cl_2	0.001	C	NONE				
HCl	0.001	C	"				
C_3H_5Cl	4	C	"				

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23	UNCON EMISS 24 30	Q 31	CEF 32 35	Q 36	SCF 37 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ____________________

RELATED INDUSTRIES

BIBLIOGRAPHY

SOURCE DATA TABULATION

INDUSTRY NO.	INDUSTRY	PRODUCT	
2818	IOC	EPICHLOROHYDRIN C_3H_5OCl	
DATE PREPARED	**PROCESS**	**SOURCE**	
10-26-71	CHLOROHYDRINATION OF ALLY CHLORIDE	HYDROLYZER	

COMPUTER CODE NOS.

SIC. NO. :	COLS. 1-4	☒	2	8	1	8
PRODUCT :	COLS. 5-8	☒		1	1	8
PROCESS :	COLS. 9-13				3	6
SOURCE :	COLS. 14-17	☒			4	0

POLLUTANT			CONTROL DEVICE				
DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
C_3H_5Cl	4	C	NONE				
Cl_2	0.001	B	"				
$C_3H_5Cl_3$	1	C	"				
HCl	0.001	B	"				
C_3H_5OCl	3	C	"				

COMPUTER CODE NOS.

PNC 18-20	CNO 21-23	UNCON EMISS 24-30	Q 31	CEF 32-35	Q 36	SCF 37-40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING

RELATED INDUSTRIES

BIBLIOGRAPHY

Product: Carbon Tetrachloride

Carbon tetrachloride is made by three industrial processes.

In 1970, approximately 40 percent of the carbon tetrachloride was made by the thermal chlorination of methane, namely:

$$4Cl_2 + CH_4 \xrightarrow{500C} CCl_4 + 4HCl$$

When methane is chlorinated, co-products such as chloroform are produced. These co-products show good growth rates. Chloroform, for example, has a 10 percent per year growth rate. Although methane chlorination does not have the best economics, continued growth of the process is forecast, because of the versatility of the process equipment and product distribution.

About 35 percent of the carbon tetrachloride was made by the thermal chlorination of propane, namely:

$$(C_3H_8) + 8Cl_2 \longrightarrow CCl_4 + C_2Cl_4 + 8HCl$$

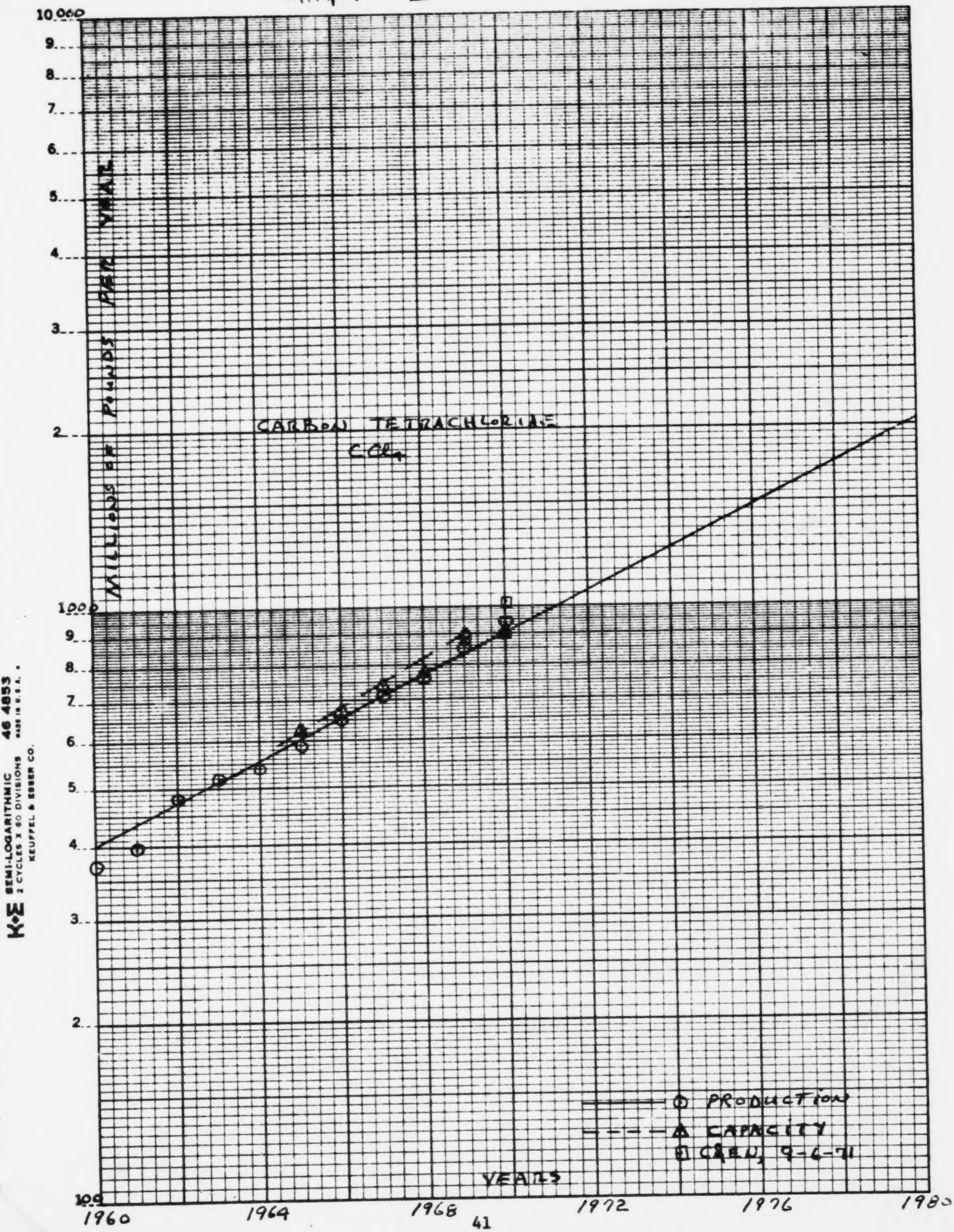
Recent developments in this process have been the use of partially chlorinated by-products, such as dichloropropane, as feed stocks. If the trend continues, this process may become dominant due to cheaper feed stocks and lower chlorine consumption.

The co-product, perchloroethylene, is a valuable product having a 1960-1970 annual growth of over 12 percent. Perchloroethylene is discussed in Section II.

Approximately 25 percent of the carbon tetrachloride, or 225 million pounds, was made by chlorinating carbon disulfide, either directly or indirectly. This is an old and declining process. Most of the disulfide plants are located in the northeast near the markets, but are being replaced by plants in the Gulf Coast area, which use cheaper feed stocks.

Carbon tetrachloride is toxic, and is used mainly as an intermediate for freons. Chart 1 shows a plot of total carbon tetrachloride production and capacity from 1960 to 1971, along with a production projection to 1980.

CHART 1


10,000
9
8
7
6
5
4
3
2
1000
9
8
7
6
5
4
3
2
100
MILLIONS OF POUNDS PER YEAR
CARBON TETRACHLORIDE
CCl_4
PRODUCTION
CAPACITY
C&EN, 9-6-71
YEARS
1960
1964
1968
1972
1976
1980
K+E SEMI-LOGARITHMIC 46 4853
2 CYCLES X 60 DIVISIONS MADE IN U.S.A.
KEUFFEL & ESSER CO.

Process: Chlorination of Methane

The process sequence requires four main steps: (1) reaction, (2) HCl recovery, (3) chlorides recovery, and (4) chlorides refining. High-purity methane, chlorine, and recycle methane are premixed and fed to the reactor. The reactor effluent, containing organic chlorides, HCl, excess methane, and only traces of chlorine, is cooled and fed to the HCl recovery system. The first column in this system is an absorber designed for efficient HCl removal. The bulk of the absorbing liquor is HCl azeotrope (about 20 percent by weight HCl). The rich acid is thus above the azeotrope and allows stripping of anhydrous HCl. The second column distills off anhydrous HCl and produces the required azeotrope in the bottoms.

The HCl-free gases from the absorber are washed with caustic soda to remove final traces of HCl and are then ready for chlorides recovery. For the intermediate product distribution under discussion, compression, cooling, and drying with sulfuric acid are an economical combination.

The reactor is operated at 15 pounds per square inch gage and 400 to 500C. The yields are over 95 percent. There is one source of air pollution. It is a purge on the recycled methane to remove inerts. The vents from the product purification system are returned to the suction side of the recycle compressor.

The raw materials are chlorine (dry gas), methane (99 percent plus), sulfuric acid, and caustic soda. The by-products are other chloromethanes, perchloroethylene, hydrogen chloride, heavy ends, and spent caustic sludge.

PR 100

FLOWSHEET

Job EPA

Location CHLORINE STUDY

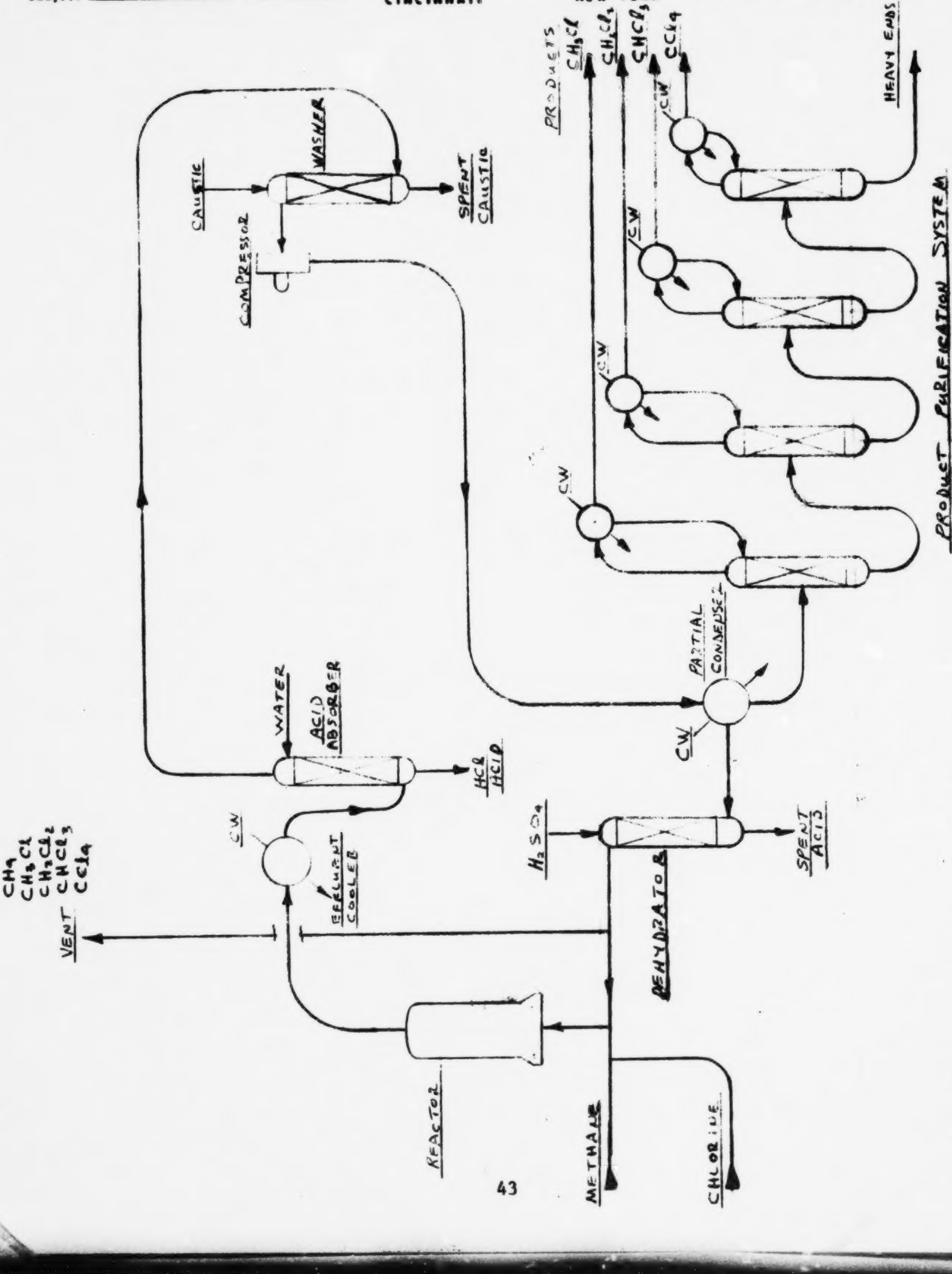
Subject CHLORIDES OF METHANE

PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING AND RESEARCH
CINCINNATI NEW YORK

File No. 03383 Sheet No. 1

Checked by ______ Date ______

Computed by SPK Date 11-3-71


PRODUCTS
CH_3Cl
CH_2Cl_2
$CHCl_3$
CCl_4
HEAVY ENDS
CW
CW
CW
CW
WASHER
CAUSTIC
SPENT CAUSTIC
COMPRESSOR
PRODUCT PURIFICATION SYSTEM
PARTIAL CONDENSER
CW
WATER
ACID ABSORBER
HCl ACID
CW
EFFLUENT COOLER
CH_4
CH_3Cl
CH_2Cl_2
$CHCl_3$
CCl_4
VENT
H_2SO_4
DEHYDRATOR
SPENT ACID
REACTOR
METHANE
CHLORINE

PROCESS: CHLORINATION OF METHANE

PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO. 2818	INDUSTRY IOC	PRODUCT CARBON TETRACHLORIDE CCl_4	
DATE: 10-27-71	PROCESS CHLORINATION OF METHANE		

COMPUTER CODE NOS.

SIC. NO. :	COLS. 1-4	☒	2	8	1	8
PRODUCT :	COLS. 5-8	☒		1	1	6
PROCESS :	COLS. 9-13				3	3

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
38	DOW	FREEPORT, TX	A	130	A
253	VULCAN	WICHITA, KS	A	25	B
53	DOW	PLAQUEMINE, LA	A	20	B

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 49	50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO. 2818	**INDUSTRY** IOC	**PRODUCT** CARBON TETRACHLORIDE CCl_4
DATE PREPARED 10-27-71	**PROCESS** CHLORINATION OF METHANE	**SOURCE** DEHYDRATOR

COMPUTER CODE NOS.

SIC. NO. :	COLS. 1-4	☒	2	8	1	8
PRODUCT :	COLS. 5-8	☒		1	1	6
PROCESS :	COLS. 9-13				3	3
SOURCE :	COLS. 14-17	☒			4	3

POLLUTANT			CONTROL DEVICE				
DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
CH_3Cl	26	C	NONE				
CH_2Cl_2	4	C	"				
CH_4	2	C	"				
CCl_4	2	C	"				
CCl_3H	2	C	"				

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23	UNCON EMISS 24 30	Q 31	CEF 32 35	Q 36	SCF 37 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING

RELATED INDUSTRIES

BIBLIOGRAPHY

Process: Thermal Chlorination of Propane

Fresh chlorine feed, together with recycled chlorine, and the propane feed are introduced into a vaporizer where they are mixed with recycled chlorides in the vapor space. The chlorine is in 10 to 25 percent excess, based on the propane. The recycle chloride diluent rate (controlled by heat input to the vaporizer) is designed to control adiabatic reactor temperature at 550 to 700C and is usually about 75 mole percent of the total stream; its composition also serves to control CCl_4-C_2Cl_4 ratio. The mixed gases, at atmospheric pressure, are fed to a refractory-lined reactor where they are rapidly mixed with the contents, thereby heated to ignition, and reacted adiabatically. The reaction is self-sustaining and supported by the considerable heat of reaction (after start-up), but is tempered and controlled by the diluent action of the recycle chlorides.

The reactor effluent is essentially free of unreacted hydrocarbon and consists mainly of carbon tetrachloride, perchloroethylene, HCl and excess chlorine. It is rapidly quenched by intimate contact with a liquid which is largely perchloroethylene. The rapid quench serves to preserve the equilibrium ratio attained in the reactor and prevents formation of undesirable by-products. It also serves to dissolve any quantities of hexachlorobenzene which may be present (these are small if reaction temperature is maintained below 650C) and which might introduce difficulties due to deposition of solids on heat transfer surfaces and in vessels. Some heat economy is obtained from the hot reactor effluent, which serves to boil the contents of the quench tank and thus provide boil-up for the CCl_4 column. Hexachlorobenzene is purged from the quench tank by allowing liquid to overflow to the recycle surge tank.

The CCl_4 column, operating on boil-up from the quench tank, returns quench liquid rich in perchloroethylene as a bottoms stream. Fractionation results in an overhead which is largely free of perchloroethylene. The condenser yields carbon tetrachloride, the desired quantity of which is withdrawn as product, the remainder being used as reflux. Chlorides-free gases (HCl and chlorine) are also disengaged at the overhead. These gases are scrubbed with water to remove HCl, the effluent liquor forming the aqueous HCl by-product. They are subsequently dried with concentrated sulfuric acid and purged to maintain the balance of inert gases; the remaining chlorine (with some uncondensed chlorides) is recycled to feed.

A perchloroethylene-rich stream is removed as a side stream from the CCl_4 column and processed to produce perchloroethylene product. Heavy ends are first removed by distillation and returned to the recycle surge tank. The overhead from the heavy ends column is fractionated in the C_2Cl_4 column where the desired quantity of perchloroethylene product is removed as the bottoms and the overhead (largely carbon tetrachloride) is sent to recycle.

The recycle surge tank serves as a reservoir for three recycle streams: (1) the quench tank overflow (largely perchloroethylene with some hexachlorobenzene), (2) heavy ends from the heavy ends column, and (3) the C_2Cl_4 column overhead (largely carbon tetrachloride). Proper control results in a recycle mixture of the desired composition, and this is fed to the vaporizer where the vapors are mixed with the feed materials.

To prevent buildup of hexachlorobenzene in the system, liquid is withdrawn from the vaporizer and sent to the heavies still. Here the more volatile components are stripped off and returned to the vaporizer, while heavy liquid consisting of hexachlorobenzene and some hexachloroethane is purged from the still pot.

The raw materials are propane, chlorine, catalyst ($CuCl_2$ and $BaCl_2$), water and sulfuric acid. The by-products are tetrachloroethylene (perchloroethylene), hexachlorobenzene, hydrogen chloride, hexachloroethane, and spent sulfuric acid.

There is one source of air pollution, the purge on the dry chlorine recycle, which removes inerts. This purge is continuous, with chlorine being the pollutant. The major cause of the pollution is impurities in the raw materials.

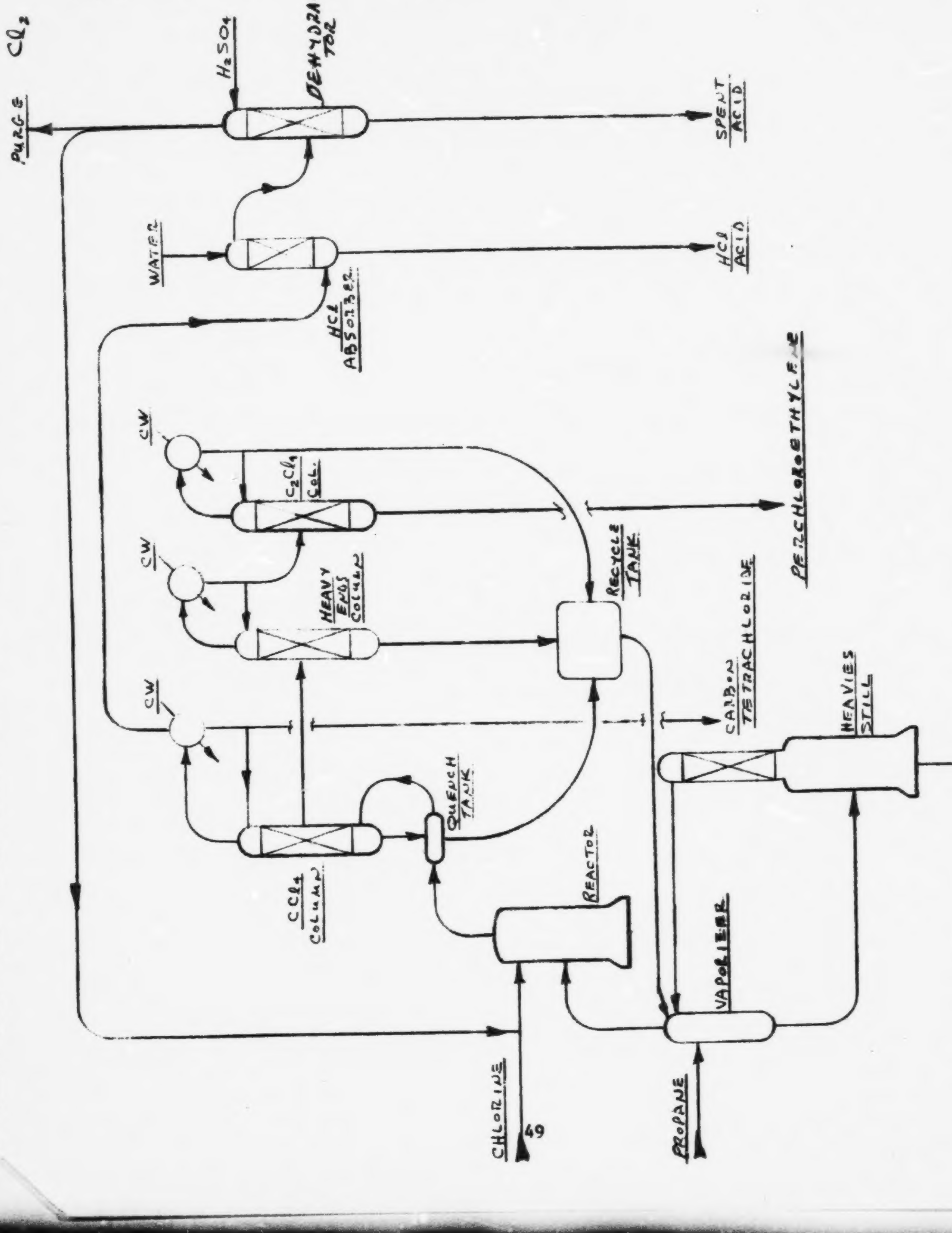
PR 109

FLOWSHEET

PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING AND RESEARCH
CINCINNATI NEW YORK

Job EPA
Location CHLORINE STUDY
Subject CARBON TETRACHLORIDE AND PERCHLOROETHYLENE

File No. 3383 Sheet No. 1
Checked by ________ Date ________
Computed by SPK Date 11-3-71


Cl_2
PURGE
H_2SO_4
DEHYDRATOR
SPENT ACID
WATER
HCl ACID
HCl ABSORBER
CW
C_2Cl_4 COL.
PERCHLOROETHYLENE
CW
HEAVY ENDS COLUMN
RECYCLE TANK
CW
CARBON TETRACHLORIDE
HEAVIES STILL
HEAVY ENDS
QUENCH TANK
CCl_4 COLUMN
REACTOR
VAPORIZER
CHLORINE
PROPANE

PROCESS: THERMAL CHLORINATION OF PROPANE

PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO. 2818	INDUSTRY IOC	PRODUCT CARBON TETRACHLORIDE CCl_4
DATE: 10-28-71	PROCESS THERMAL CHLORINATION OF PROPANE	

COMPUTER CODE NOS.

SIC. NO. :	COLS. 1-4	☒	2	8	1	8
PRODUCT :	COLS. 5-8	☒		1	1	6
PROCESS :	COLS. 9-13				3	5

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
21	DOW	PITTSBURG, CA	A	45	B
266	STAUFFER	LEMOYNE, AL	A	130	C
53	VULCAN	GEISMAR, LA	A	35	B

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 49	50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

3/3

INDUSTRY NO. 2818	**INDUSTRY** IOC	**PRODUCT** CARBON TETRACHLORIDE CCl_4	**COMPUTER CODE NOS.**
DATE PREPARED 10-28-71	**PROCESS** THERMAL CHLORINATION OF PROPANE	**SOURCE** DEHYDRATOR	

COMPUTER CODE NOS.						
SIC. NO.	COLS. 1-4	☒	2	8	1	8
PRODUCT	COLS. 5-8	☒		1	1	6
PROCESS	COLS. 9-13				3	5
SOURCE	COLS. 14-17	☒			4	3

POLLUTANT / CONTROL DEVICE

DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
Cl_2	20	C	NONE				

COMPUTER CODE NOS.

PNO 18-20	CNO 21-23	UNCON EMISS 24-30	Q 31	CEF 32-35	Q 36	SCF 37-40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING

RELATED INDUSTRIES

BIBLIOGRAPHY

Process: Carbon Disulfide Chlorination

Industrially, both direct and indirect chlorination of carbon disulfide are employed. In a direct chlorination process, a mixture of carbon tetrachloride, carbon disulfide and sulfur chlorides, recycled from a subsequent process step, is directly contacted with excess chlorine at about 30C over a divided iron catalyst, converting over 99 percent of the carbon disulfide to carbon tetrachloride. Some fresh carbon disulfide feed may also be diverted to the primary chlorinator for purposes of controlling downstream loads. It is essential that the reaction be complete but that over-chlorination of sulfur to sulfur monochloride be avoided to prevent appearance of carbon disulfide and sulfur monochloride in the distilled crude product. Distillation of the reactor effluent yields a bottoms product and an overhead product of relatively pure carbon tetrachloride. This material may be treated with a base to destroy sulfur chlorides, and dried.

An indirect chlorination process is similar. Fresh carbon disulfide feed reacts with sulfur monochloride under conditions such that the carbon disulfide is all but completely reacted. However, the reactor product contains a fraction of a percent of carbon disulfide, as well as carbon tetrachloride and sulfur. A direct-chlorination polishing reactor is used to convert this remaining carbon disulfide and to facilitate the subsequent distillation, where crude carbon tetrachloride is removed overhead and molten sulfur containing some sulfur monochloride is the bottoms product. The crude carbon tetrachloride may be purified as in the direct chlorination process, an alcoholic caustic treatment with redistillation is shown on the flow sheet. Sulfur equivalent to the fresh carbon disulfide feed is separated from the bottoms product and may be returned to the CS_2 plant for processing. The residual sulfur stream is directly chlorinated to provide the sulfur chlorides chlorinating agent for the first reaction stage. The flow sheet shows the indirect process.

The raw materials are carbon disulfide, chlorine, iron catalyst, and caustic soda. The by-products are heavy ends, sulfur chlorides, sulfur, and spent caustic sludge.

The quantities of air pollutants from the chlorination of carbon disulfide are very small. The neutralizer-dryer, using caustic soda, absorbs most of the noncondensables such as carbon dioxide or excess chlorine. The vacuum jets on the product still are vented back into the neutralizer-dryer.

FLOWSHEET

FR 109

Job EPA

Location CHLORINE STUDY

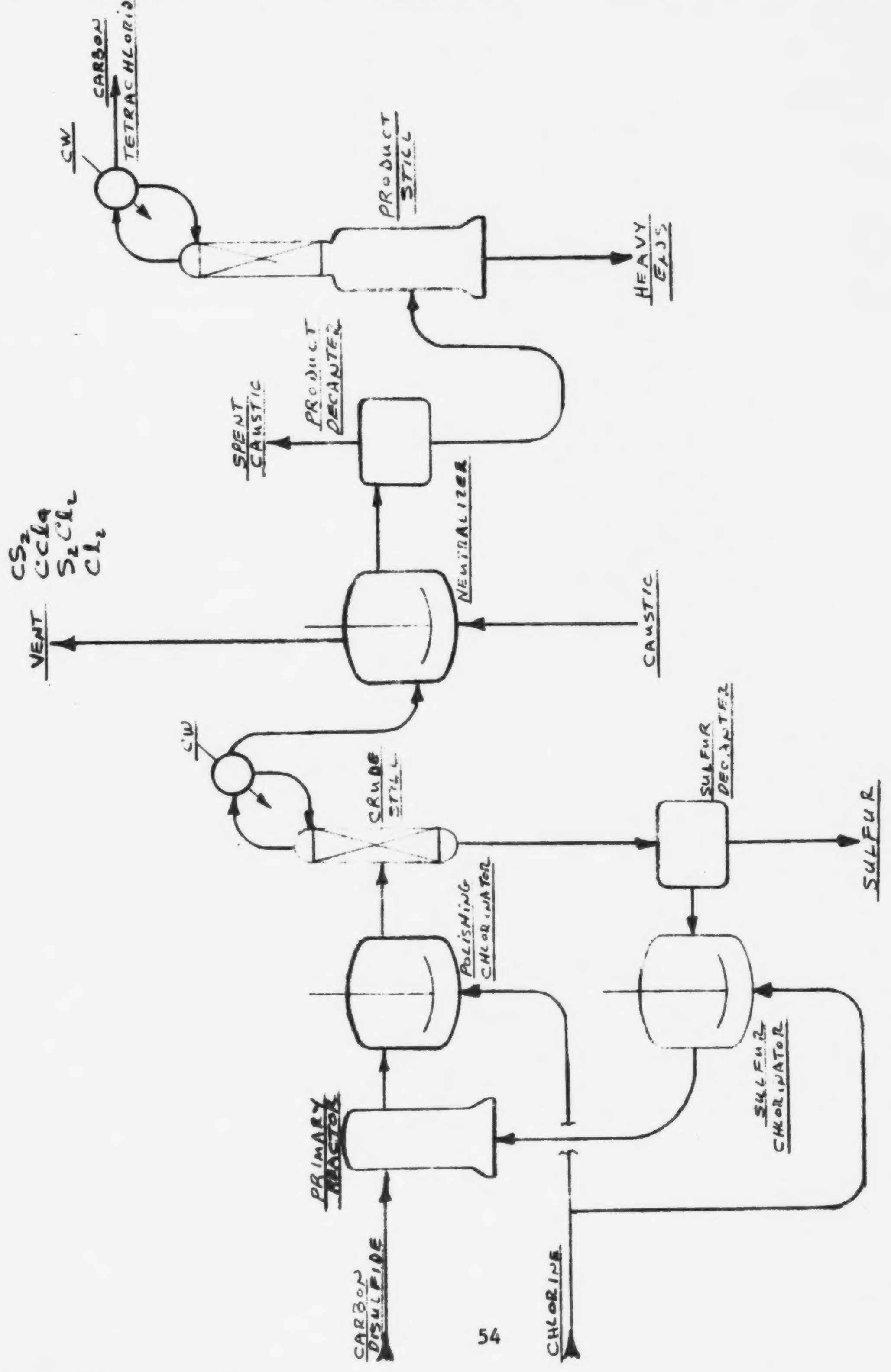
Subject CARBON TETRACHLORIDE

PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING
AND RESEARCH
CINCINNATI NEW YORK

File No. 3383 Sheet No 1

Checked by ______ Date ______

Computed by SPK Date 11-3-71


CW
CARBON TETRACHLORIDE
PRODUCT STILL
HEAVY ENDS
PRODUCT DECANTER
SPENT CAUSTIC
CS_2
CCl_4
S_2Cl_2
Cl_2
VENT
NEUTRALIZER
CAUSTIC
CW
CRUDE STILL
SULFUR DECANTER
SULFUR
POLISHING CHLORINATOR
SULFUR CHLORINATOR
PRIMARY REACTOR
CARBON DISULFIDE
CHLORINE

PROCESS: CHLORINATION OF CARBON DISULFIDE

PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO. 2818	INDUSTRY IOC	PRODUCT CARBON TETRACHLORIDE CCl_4
DATE: 10-25-71	PROCESS CHLORINATION OF CARBON DISULFIDE	

COMPUTER CODE NOS.

SIC. NO.	: COLS. 1-4	☒	2	8	1	8
PRODUCT	: COLS. 5-8	☒		1	1	6
PROCESS	: COLS. 9-13				3	4

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
233	FMC - ALLIED	SO. CHARLESTON, WV	A	225	B
24	STAUFFER	NIAGARA FALLS, NY	A	150	B
35	STAUFFER	LOUISVILLE, KY	A	70	B
220	DIAMOND	PAINESVILLE, OH	A	30	B

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 49	50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO. 2818	**INDUSTRY** IOC	**PRODUCT** CARBON TETRACHLORIDE CCl_4	
DATE PREPARED 10-15-71	**PROCESS** CHLORINATION OF CARBON DISULFIDE	**SOURCE** NEUTRALIZER	

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒	2	8	1	8
PRODUCT : COLS. 5-8	☒		1	1	6
PROCESS : COLS. 9-13				3	4
SOURCE : COLS. 14-17	☒			2	7

POLLUTANT			CONTROL DEVICE				
DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
CS_2	4	C	AFTER COOLER	0.50	C	0	C
CCl_4	28	C	"	0.50	C	0	C
S_2Cl_2	2	C	"	0.67	C	0	C
Cl_2	0.0003	B					

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23	UNCON EMISS 24 30	Q 31	CEF 32 35	Q 36	SCF 37 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ________________

RELATED INDUSTRIES

BIBLIOGRAPHY

Product: Propylene Oxide

Starting in the early sixties, there was a rapid growth in the capacity for propylene oxide (PO) as the chlorohydrin plants for ethylene oxide were modified for PO production. The production growth rate exceeds 10 percent per year. Shown on Chart 5 are the production and capacities for PO, from 1960 to 1970. A projection indicates a 1980 production of over 3000 million pounds.

The two industrial reaction steps for making PO are as follows:

Chlorohydrination:

$$C_3H_6 + HOCl \longrightarrow C_3H_6(OH)Cl$$

Hydrolysis:

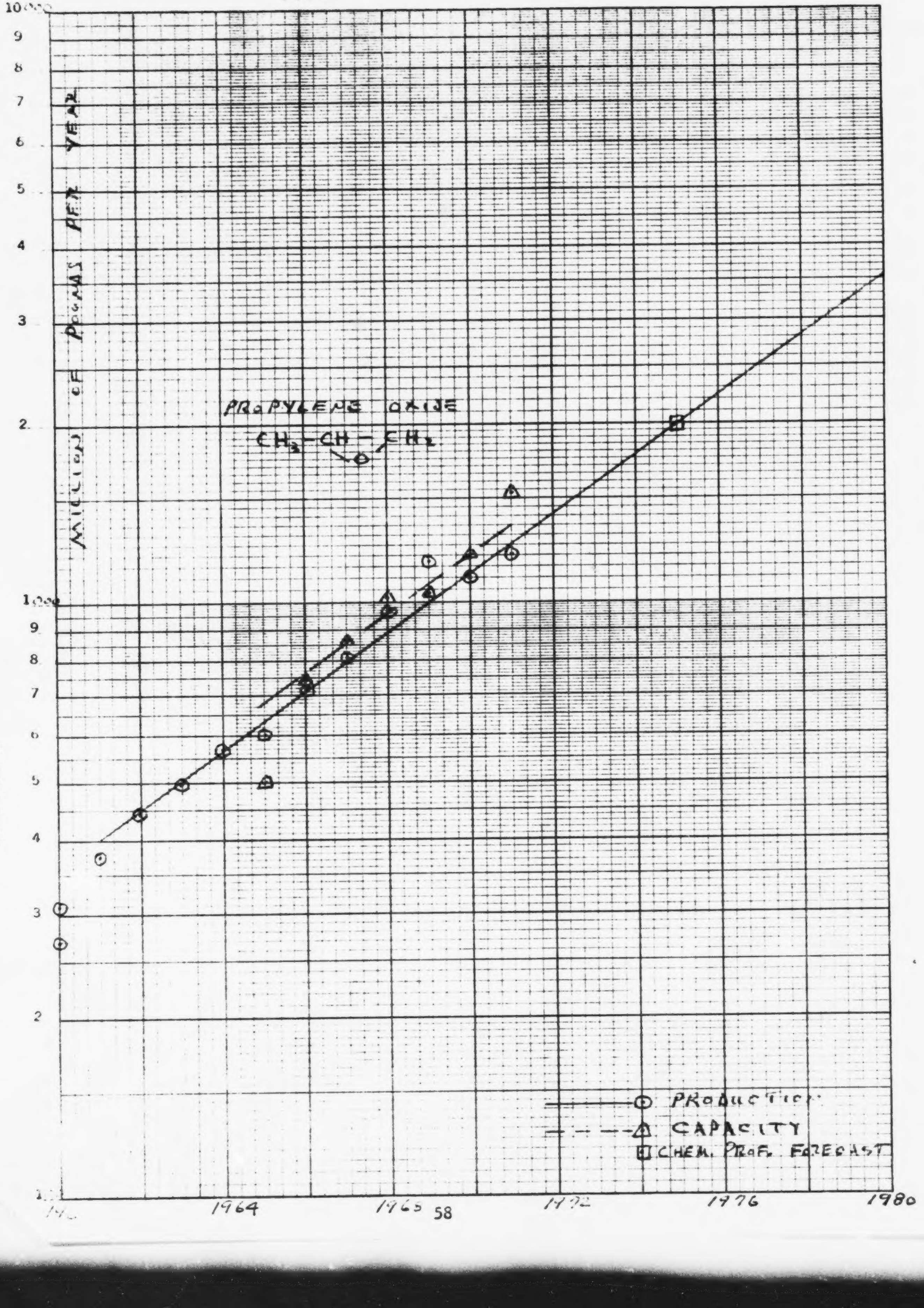
$$C_3H_6(OH)Cl + 1/2\ CaOH \longrightarrow 1/2\ CaCl_2 + H_2O + CH_6O$$

Though a direct oxidation plant (known as the Oxirane process) has been built in Texas for the production of 170 million pounds of PO per year, great expansion of this process in the seventies is not expected. However, after 1980, the Oxirane process will probably dominate. The reaction is:

$$C_3H_6 + 1/2\ O_2 \longrightarrow C_3H_6O$$

The main use of PO is an intermediate for making polyols.

CHART 5



MILLION OF POUNDS PER YEAR
10,000
9
8
7
6
5
4
3
2
1,000
9
8
7
6
5
4
3
2
PROPYLENE OXIDE
$CH_3-CH-CH_2$
O
PRODUCTION
CAPACITY
CHEM. PROF. FORECAST
1960
1964
1968
1972
1976
1980
485
KEUFFEL & ESSER CO.

Process: Chlorohydrination of Propylene, then Hydrolysis

Propylene, chlorine, and water are introduced into the bottom of a packed tower where they react under controlled conditions to form propylene chlorohydrin. The chlorine/propylene/water ratio of the feed to the tower is so chosen that the liquid effluent leaving the tower contains about 5 percent propylene chlorohydrin. The temperature of the effluent from the tower is about 50C, and the pressure is atmospheric. Yields of chlorohydrin are about 90 percent. Unreacted propylene, which is in excess in the tower feed, leaves the top of the tower and is scrubbed with a dilute caustic solution to remove hydrochloric acid and any residual chlorine, and then is recycled. A portion of the recycled propylene is vented to control inert gases.

The liquid stream leaving the chlorohydrin tower is pumped to the flash hydrolyzer, where the chlorohydrin solution is mixed with an excess (10 to 20 percent) of 10 percent solution of milk of lime. By heating the mixture with live steam at about 100C and in a vacuum of 1.5 pounds per square inch absolute, the PO is removed from the hydrolysis zone as it forms. The vapors are partially cooled to remove part of the water, and then sent to dual distillation columns to separate the PO out overhead. The bottoms are mostly water and dichloropropane.

Yields of PO, based on the entering propylene, are about 80 percent with dichloropropane the main by-product. The other by-products are sodium chloride, calcium chloride, chloropropenes, and heavies. The raw materials are propylene, chlorine, water, lime, and caustic soda.

The hydrolyzer is vented back into the lime feed system.

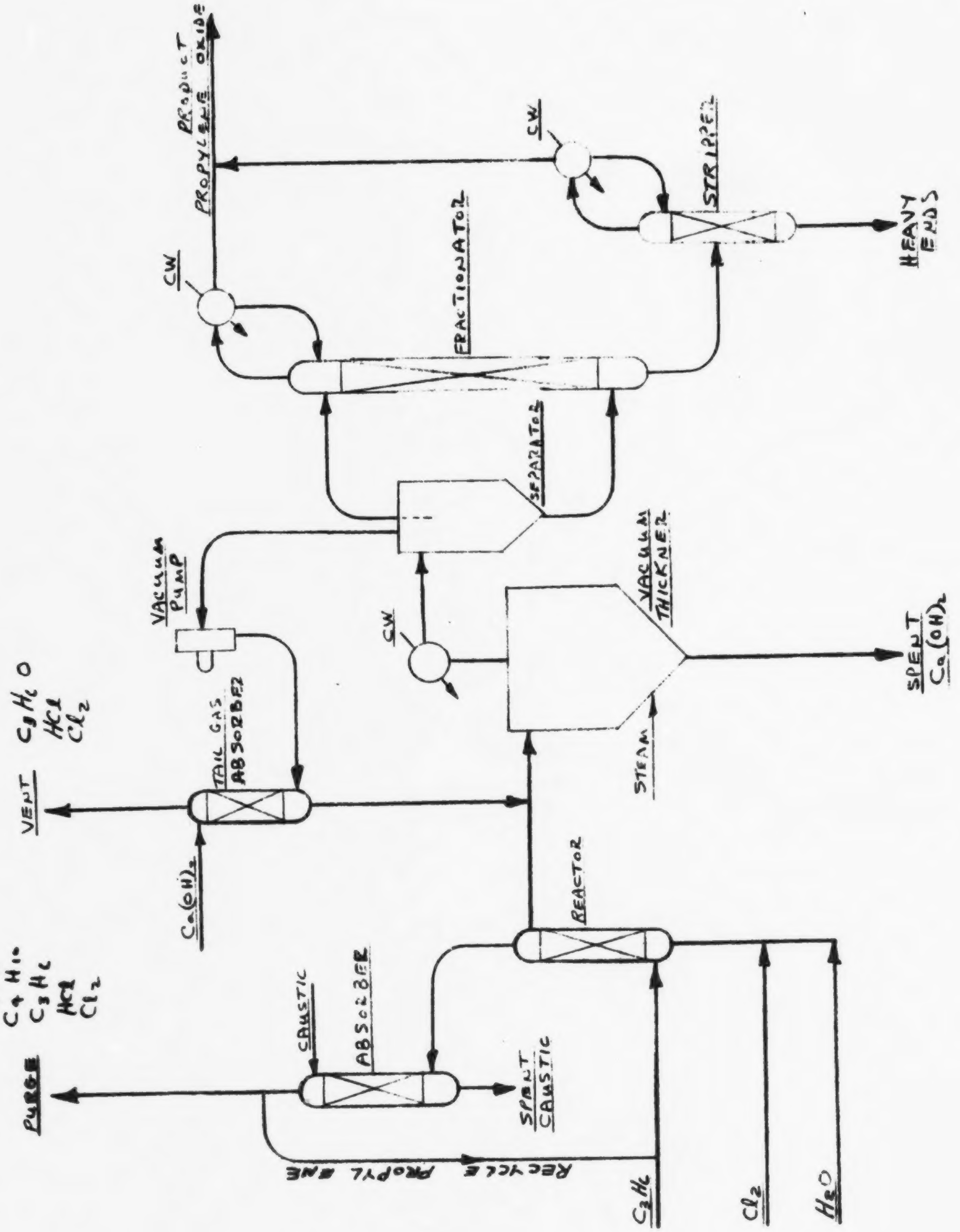
PR 109

FLOWSHEET

PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING
AND RESEARCH
CINCINNATI NEW YORK

Job EPA
Location CHLORINE STUDY
Subject PROPYLENE OXIDE

File No. 3383 Sheet No. ______
Checked by ______ Date ______
Computed by SPK Date 11-4-71



PURGE
C_2H_6
C_4H_{10}
C_3H_6
HCl
Cl_2
CAUSTIC
ABSORBER
SPENT CAUSTIC
RECYCLE PROPYLENE
C_3H_6
Cl_2
H_2O
REACTOR
$Ca(OH)_2$
VENT
TAIL GAS ABSORBER
C_3H_6O
HCl
Cl_2
VACUUM PUMP
CW
VACUUM THICKNER
STEAM
SPENT $Ca(OH)_2$
SEPARATOR
FRACTIONATOR
CW
PRODUCT PROPYLENE OXIDE
CW
STRIPPER
HEAVY ENDS

PROCESS: CHLOROHYDRINATION OF PROPYLENE, THEN HYDROLYSIS.

PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO.	INDUSTRY	PRODUCT
2818	IOC	PROPYLENE OXIDE C_3H_6O

DATE:	PROCESS
10-26-71	CHLOROHYDINATION OF PROPYLENE FOLLOWED BY HYDROLYSIS

COMPUTER CODE NOS.

SIC. NO. :	COLS. 1-4	☒	2	8	1	8
PRODUCT :	COLS. 5-8	☒		1	2	7
PROCESS :	COLS. 9-13				4	3

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
136	CELANESE	BISHOP, TX	A	10	A
53	JEFFERSON	PORT NECHES, TX	A	110	A
193	OLIN	BRANDENBURG, KY	A	120	A
233	UNION CARBIDE	So. CHARLESTON, WV	A	200	A
37	WYANDOTTE	WYANDOTTE, MI	A	200.	A
38	DOW	FREEPORT, TX	A	650	A
195	DOW	MIDLAND, MI	A	40	A
53	DOW	PLAQUEMINE, LA	A	200	A

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 49	☒ 50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

1/2

INDUSTRY NO. 2818	**INDUSTRY** IOC	**PRODUCT** PROPYLENE OXIDE C_3H_6O	**COMPUTER CODE NOS.**
DATE PREPARED 10-26-71	**PROCESS** CHLOROHYDRINATION OF PROPYLENE THEN HYDROLYSIS	**SOURCE** ABSORBER	

COMPUTER CODE NOS.

SIC. NO.	: COLS. 1-4	☒	2	8	1	8
PRODUCT	: COLS. 5-8	☒		1	2	7
PROCESS	: COLS. 9-13				4	3
SOURCE	: COLS. 14-17	☒				1

POLLUTANT / CONTROL DEVICE

DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
C_2H_6	17	C	NONE				
C_4H_{10}	17	C	"				
C_3H_6	17	C	"				
HCl	0.001	C	"				
Cl_2	0.001	C	"				

COMPUTER CODE NOS.

PNO 18-20	CNO 21-23	UNCON EMISS 24-30	Q 31	CEF 32-35	Q 36	SCF 37-40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ______

RELATED INDUSTRIES

BIBLIOGRAPHY

SOURCE DATA TABULATION

2/2

INDUSTRY NO. 2818	**INDUSTRY** IOC	**PRODUCT** PROPYLENE OXIDE C_3H_6O	
DATE PREPARED 11-4-71	**PROCESS** CHLOROHYDRINATION OF PROPYLENE THEN HYDROLYSIS	**SOURCE** TAIL GAS ABSORBER	

COMPUTER CODE NOS.

SIC. NO. :	COLS. 1-4	X	2	8	1	8
PRODUCT :	COLS. 5-8	X		1	2	7
PROCESS :	COLS. 9-13				4	3
SOURCE :	COLS. 14-17	X			4	1

POLLUTANT			CONTROL DEVICE				
DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
C_3H_6O	8.2	C	NONE				
HCl	0.001	C	"				
Cl_2	0.001	C	"				

COMPUTER CODE NOS.

PNO 18-20	CNO 21-23	UNCON EMISS 24-30	Q 31	CEF 32-36	Q 36	SCF 37-40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING

RELATED INDUSTRIES

BIBLIOGRAPHY

Product: Ethyl Chloride

In 1970, over 80 percent of the ethyl chloride was made by hydrochlorinating ethylene in this liquid phase reaction:

$HCl + C_2H_4 \longrightarrow C_2H_5Cl$

The remaining ethyl chloride was made by these two reactions:

Thermal chlorination of ethane:

$Cl_2 + C_2H_6 \longrightarrow C_2H_5Cl + HCl$

Hydrochlorination of ethanol:

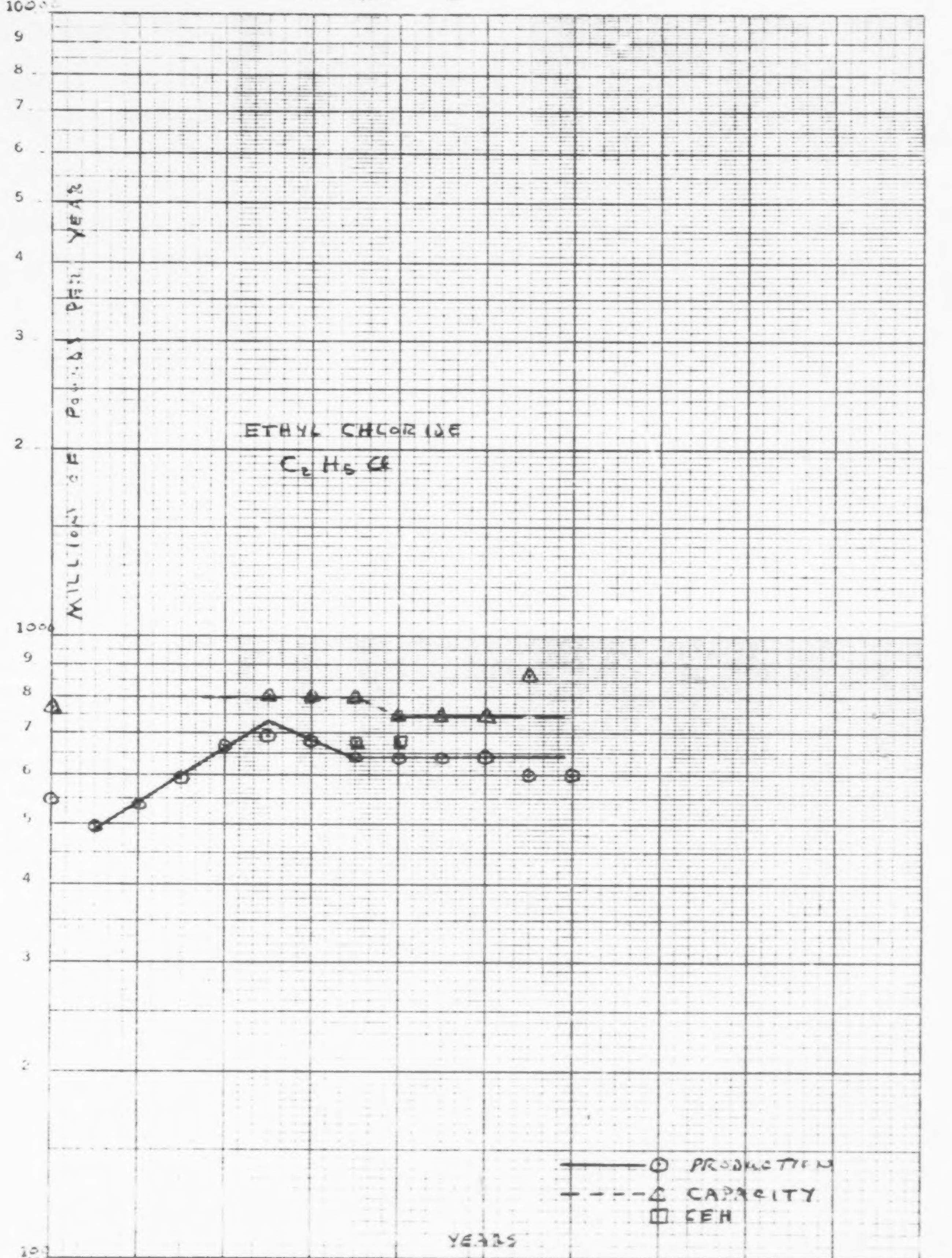
$HCl + C_2H_5OH \longrightarrow C_2H_5Cl + H_2O$

The first of these reactions is handicapped by high-cost chlorine and lower yields. The second is almost completely obsolete, due to the high-cost ethanol, although the yields are very good.

The capacity and production of ethyl chloride is declining very slowly. The decline is probably due to the reduction in the use of tetraethyl lead. However, the decline is offset by the increasing use of gasoline. It is estimated that the production will stay at 640 million pounds per year through 1980. See Chart 6 for production and capacities from 1960 to 1970.

The main use of ethyl chloride is as an intermediate for making tetraethyl lead. This use is in decline due to tetramethyl lead growth and the environmentalists fight against "leaded" gasolines.

CHART 6


MILLIONS OF POUNDS PER YEAR
ETHYL CHLORIDE
C_2H_5Cl
1000
9
8
7
6
5
4
3
2
100
YEARS
1972
1976
1980
PRODUCTION
CAPACITY
CEH

Process: Hydrochlorination of Ethylene

Ethyl chloride is produced by addition of hydrogen chloride to ethylene under anhydrous conditions in the presence of a catalyst such as aluminum chloride.

Ethylene gas and substantially anhydrous hydrogen chloride are mixed in approximately equimolecular proportions and passed into a reactor partially filled with ethylene dichloride or a mixture of ethyl chloride and ethylene dichloride. In the presence of 0.2 to 0.3 percent aluminum chloride, at a temperature of 35 to 40C, and a pressure of 40 pounds per square inch gage, the exothermic hydrochlorination takes place. The vaporized products are fed into a column or "flash drum," where the lower boiling ethyl chloride is separated from the heavier polymers. The crude ethyl chloride is refined by fractionation. Catalyst is continually withdrawn, and new makeup catalyst is added.

The overall yield based on ethylene is about 90 percent.

The raw materials are ethylene, hydrogen chloride, and aluminum chloride catalyst. The main by-product is ethylene polymer oil.

The only vent on the process is a purge on the recycled ethylene system, which keeps inerts (such as CO_2 and CH_4) from building up.

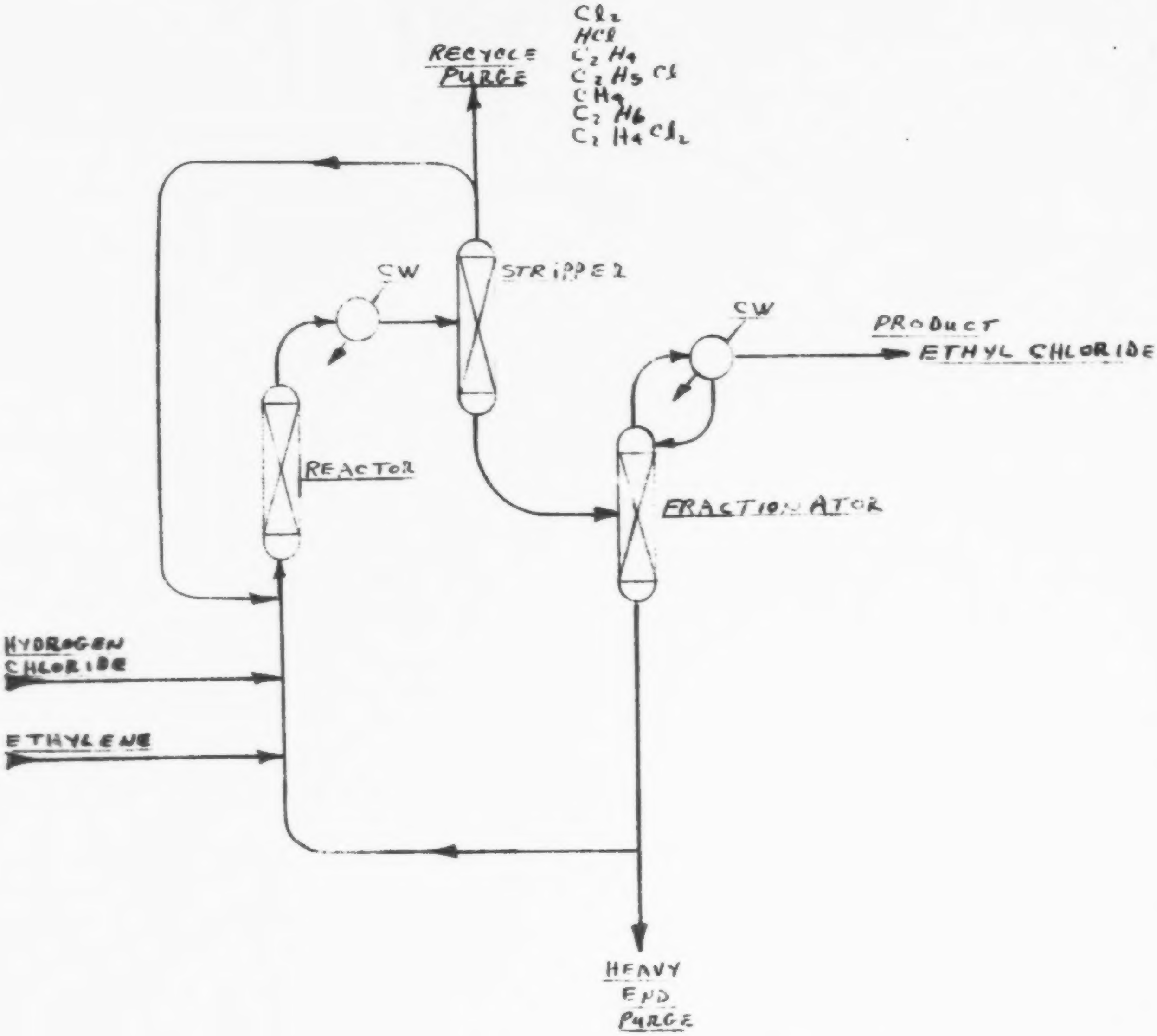
PR 109

FLOWSHEET

PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING
AND RESEARCH
CINCINNATI NEW YORK

Job EPA
Location CHLORINE STUDY
Subject ETHYL CHLORIDE

File No. 03383 Sheet No 1
Checked by ____ Date ____
Computed by SPK Date 11-3-71


RECYCLE
PURGE
Cl_2
HCl
C_2H_4
C_2H_5Cl
CH_4
C_2H_6
$C_2H_4Cl_2$
SW
STRIPPER
SW
PRODUCT
ETHYL CHLORIDE
REACTOR
FRACTIONATOR
HYDROGEN
CHLORIDE
ETHYLENE
HEAVY
END
PURGE

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PROCESS: HYDROCHLORINATION OF ETHYLENE

PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO.	INDUSTRY	PRODUCT
2818	IOC	ETHYL CHLORIDE C_2H_5Cl

DATE:	PROCESS
10-27-71	HYDROCHLORINATION OF ETHYLENE

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒	2	8	1	8	
PRODUCT : COLS. 5-8	☒		1	1	9	
PROCESS : COLS. 9-13				3	7	

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
17	AMERCHEM	LONG BEACH, CA	A	100	A
53	ETHYL	BATON ROUGE, LA	A	270	A
38	ETHYL	HOUSTON, TX	A	100	A
263	NATIONAL DISTILL.	TUSCOLA, IL	A	60	B
53	PPG	LAKE CHARLES, LA	A	110	A
38	SHELL	HOUSTON, TX	A	85	A

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 49	50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO. 2818	**INDUSTRY** IOC	**PRODUCT** ETHYL CHLORIDE C_2H_5Cl	**COMPUTER CODE NOS.**
DATE PREPARED 10-27-71	**PROCESS** HYDROCHLORINATION OF ETHYLENE	**SOURCE** STRIPPER	

COMPUTER CODE NOS.					
SIC. NO. : COLS. 1-4	☒	2	8	1	8
PRODUCT : COLS. 5-8	☒		1	1	9
PROCESS : COLS. 9-13				3	7
SOURCE : COLS. 14-17	☒			3	6

POLLUTANT / CONTROL DEVICE

DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
Cl_2	0.001	C	NONE				
HCl	0.001	C	"				
C_2H_4	5	C	"				
C_2H_5Cl	5	C	"				
CH_4	5	C	"				
C_2H_6	5	C	"				
$C_2H_4Cl_2$	12	C	"				

COMPUTER CODE NOS.

PNO 18-20	CNO 21-23	UNCON EMISS 24-30	Q 31	CEF 32-35	Q 36	SCF 37-40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ____________

RELATED INDUSTRIES

BIBLIOGRAPHY

Process: Chlorination of Ethane

Ethyl chloride is produced by the thermal chlorination of ethane:

$$Cl + C_2H_6 \longrightarrow C_2H_5Cl + HCl$$

After preheating the ethane, equimolecular mixtures of ethane and chlorine are reacted in the vapor phase in a tank reactor at 375 to 475C and 15 to 50 pounds per square inch gage to yield about 75 percent ethyl chloride. The reacted mixture is quenched, scrubbed for HCl removal, dried, the excess ethane stripped off and the crude ethyl chloride fractionated. The excess ethane is recycled.

The raw materials are ethane and chlorine. The main by-product is dichloroethane. The purge on the recycled ethane is the only source of air pollutants.

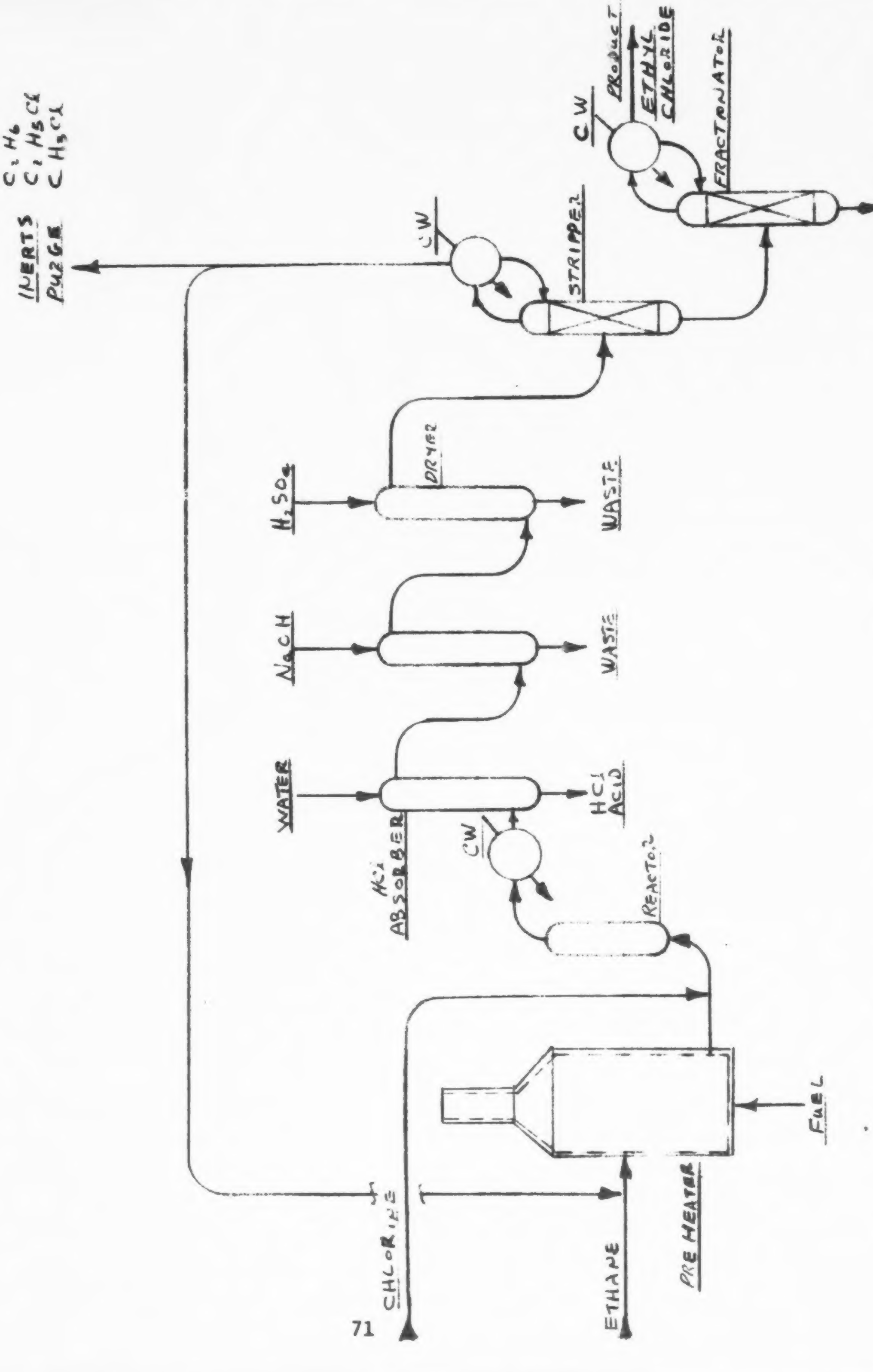
FR 100

FLOW SHEET

PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING AND RESEARCH
CINCINNATI NEW YORK

Job EPA
Location CHLORINE STUDY
Subject ETHYL CHLORIDE

File No. 03383 Sheet No. 1
Checked by ______ Date ______
Computed by SPK Date 11-22-71


CHLORINE
ETHANE
PRE HEATER
FUEL
REACTOR
CW
HCl ABSORBER
WATER
HCl Acid
NaOH
WASTE
H2SO4
DRYER
WASTE
STRIPPER
CW
INERTS PURGE
C2H6
C2H5Cl
C2H5Cl
FRACTIONATOR
CW
PRODUCT
ETHYL CHLORIDE
HEAVIES

PROCESS: CHLORINATION OF ETHANE

PROCESS DATA TABULATION

SH ____ OF ____

SIC. NO. 2818	INDUSTRY IOC	PRODUCT ETHYL CHLORIDE
DATE: 11-22-71	PROCESS CHLORINATION OF ETHANE	

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒	2	8	1	8
PRODUCT : COLS. 5-8	☒		1	1	9
PROCESS : COLS. 9-13				3	9

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
38	Dow	FREEPORT, TX	A	75	B

COMPUTER CODE NOS.

AQCR 19-22	STATE 23-24	CITY 25-36	COMPANY 37-49	50-51	CAPACITY 52-55	Q 56	YEAR 57-58

MISCELLANEOUS

RELATED SIC. NOS:

2-3

SOURCE DATA TABULATION

INDUSTRY NO. 2818	**INDUSTRY** IOC	**PRODUCT** ETHYL CHLORIDE	
DATE PREPARED 11-20-71	**PROCESS** CHLORINATION OF ETHANE	**SOURCE** STRIPPER	

COMPUTER CODE NOS.

SIC. NO. :	COLS. 1-4	☒	2	8	1	8
PRODUCT :	COLS. 5-8	☒		1	1	9
PROCESS :	COLS. 9-13				3	9
SOURCE :	COLS. 14-17	☒			3	6

POLLUTANT			CONTROL DEVICE				
DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
C_2H_6	21	C	NONE				
C_2H_5Cl	NIL	C	"				
CH_3Cl	12	C	"				

COMPUTER CODE NOS.

PNO 18-20	CNO 21-23	UNCON EMISS 24-30	Q 31	CEF 32-35	Q 36	SCF 37-40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ____

RELATED INDUSTRIES

BIBLIOGRAPHY

Process: Hydrochlorination of Ethanol

The reaction of ethyl alcohol and hydrogen chloride in the presence of a catalyst yields ethyl chloride.

Warm 95 percent ethyl alcohol is fed into the bottom of a jacketed glass-lined reactor containing a 45 percent aqueous zinc chloride solution. Countercurrent to the alcohol, substantially anhydrous hydrogen chloride is fed into the aqueous zinc chloride solution, which is maintained at about 145C. The rates of feed are approximately 0.17 and 0.13 parts per hour per part of zinc chloride solution for the alcohol and hydrogen chloride, respectively. The reactor pressure is maintained at 30 pounds per square inch. The catalyst concentration remains about constant, while vapors of ethyl chloride, water, and some hydrogen chloride are withdrawn from the reactor and passed countercurrent to a stream of water at 80C in a glass-lined scrubber. The scrubber, operating at about 30 pounds per square inch, removes the free acid from the incoming vapors. The scrubbed vapors are cooled to about 20C; at the condenser pressure (30 pounds per square inch) substantially complete condensation takes place. The liquid is passed into a decanter where ethyl chloride is separated from water. The process operates continuously to produce 99 percent ethyl chloride in a yield of 95 to 98 percent based on ethyl alcohol.

The raw materials are ethanol, zinc chloride catalyst, and HCl. The by-products are small and unimportant. The vent on the condenser is the only source of air pollutants.

PR 109

FLOW SHEET

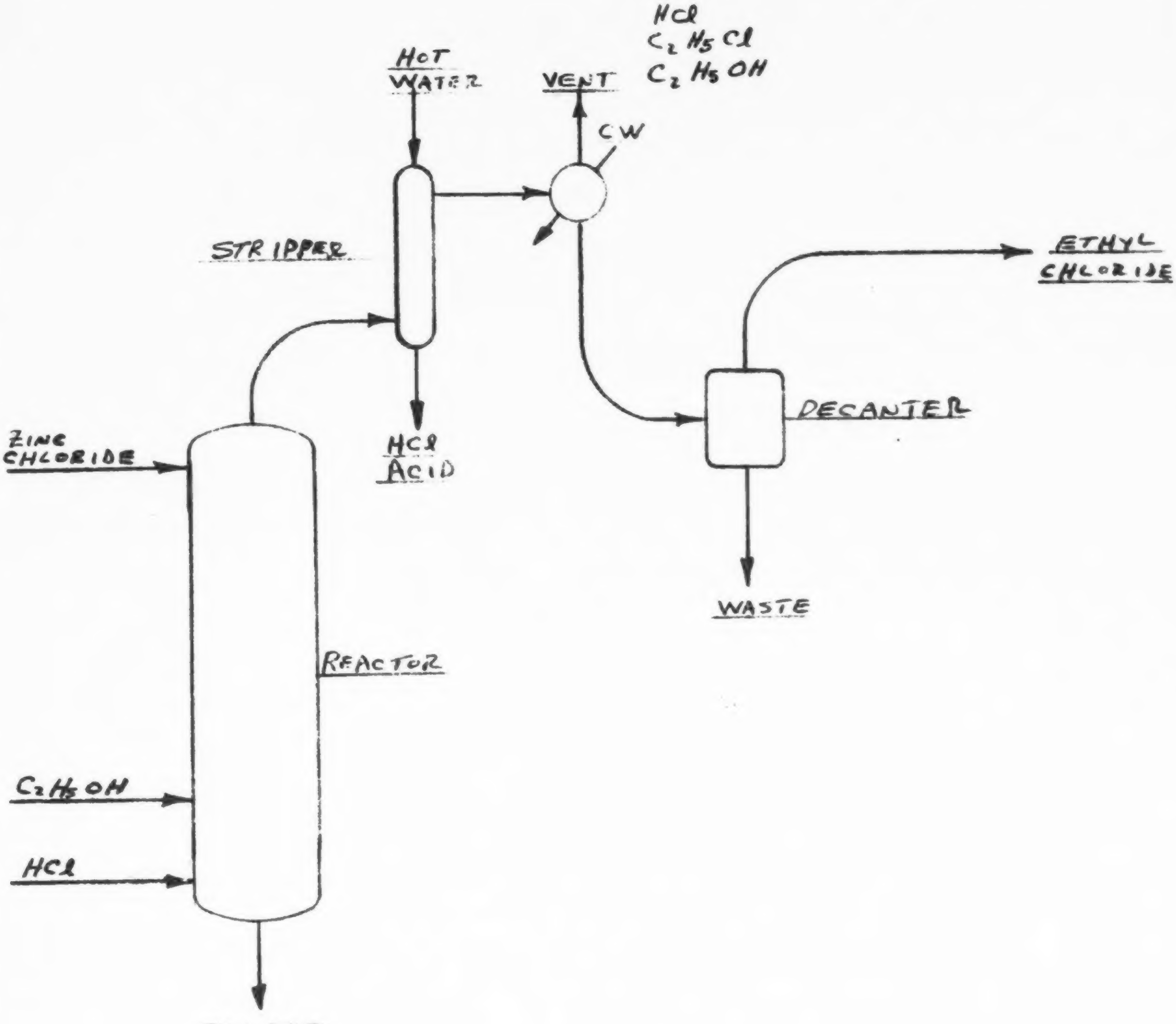
PROCESSES RESEARCH, INC.

INDUSTRIAL PLANNING
AND RESEARCH

CINCINNATI NEW YORK

Job EPA
Location CHLORINE STUDY
Subject ETHYL CHLORIDE

File No. 03383 Sheet No. 1
Checked by ______ Date ______
Computed by SPK Date 11-22-71


HCl
C_2H_5Cl
C_2H_5OH
HOT WATER
VENT
CW
STRIPPER
ETHYL CHLORIDE
DECANTER
ZINC CHLORIDE
HCl ACID
WASTE
REACTOR
C_2H_5OH
HCl
SLUDGE

PROCESS: HYDROCHLORINATION OF ETHANOL

PROCESS DATA TABULATION

SH____ OF______

SIC. NO.	INDUSTRY	PRODUCT
2818	IOC	ETHYL CHLORIDE

DATE:	PROCESS
11-22-71	HYDROCHLORINATION OF ETHANOL

COMPUTER CODE NOS.

SIC. NO. :	COLS. 1-4	☒	2	8	1	8
PRODUCT :	COLS. 5-8	☒		1	1	9
PROCESS :	COLS. 9-13				6	5

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
15	DuPONT	DEEPWATER, NJ	A	100	B
145	HERCULES	HOPEWELL, VA	A	25	A

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 49	☒ 50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO. 2818	**INDUSTRY** IOC	**PRODUCT** ETHYL CHLORIDE	**COMPUTER CODE NOS.**
DATE PREPARED 11-20-71	**PROCESS** HYDROCHLORINATION OF ETHANOL	**SOURCE** STRIPPER	

COMPUTER CODE NOS.						
SIC. NO. :	COLS. 1-4	☒	2	8	1	8
PRODUCT :	COLS. 5-8	☒		1	1	9
PROCESS :	COLS. 9-13				6	5
SOURCE :	COLS. 14-17	☒			3	6

POLLUTANT			CONTROL DEVICE				
DESCRIPTION	**EMISSION FACTOR**	**Q**	**TYPE**	**EFF. FACTOR**	**Q**	**SOURCE FACTOR**	**Q**
C_2H_5Cl	40	C	NONE				
HCl	0.02	C	"				
C_2H_5OH	2	C	"				

COMPUTER CODE NOS.

PNO 18-20	CNO 21-23	UNCON EMISS 24-30	Q 31	CEF 32-35	Q 36	SCF 37-40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ____________________

RELATED INDUSTRIES

BIBLIOGRAPHY

Product: 1,1,1-Trichloroethane

The fine solvent properties of 1,1,1-trichloroethane (TCE) have long been known, but in the past TCE has been difficult to make. With cheap vinyl chloride (about 5 cents per pound), the growth of TCE has been about 23 percent per year. See Chart 7 for production data.

TCE is made in two steps. First, vinyl chloride is hydrochlorinated in the liquid phase:

$$HCl + C_2H_3Cl \longrightarrow C_2H_4Cl_2$$

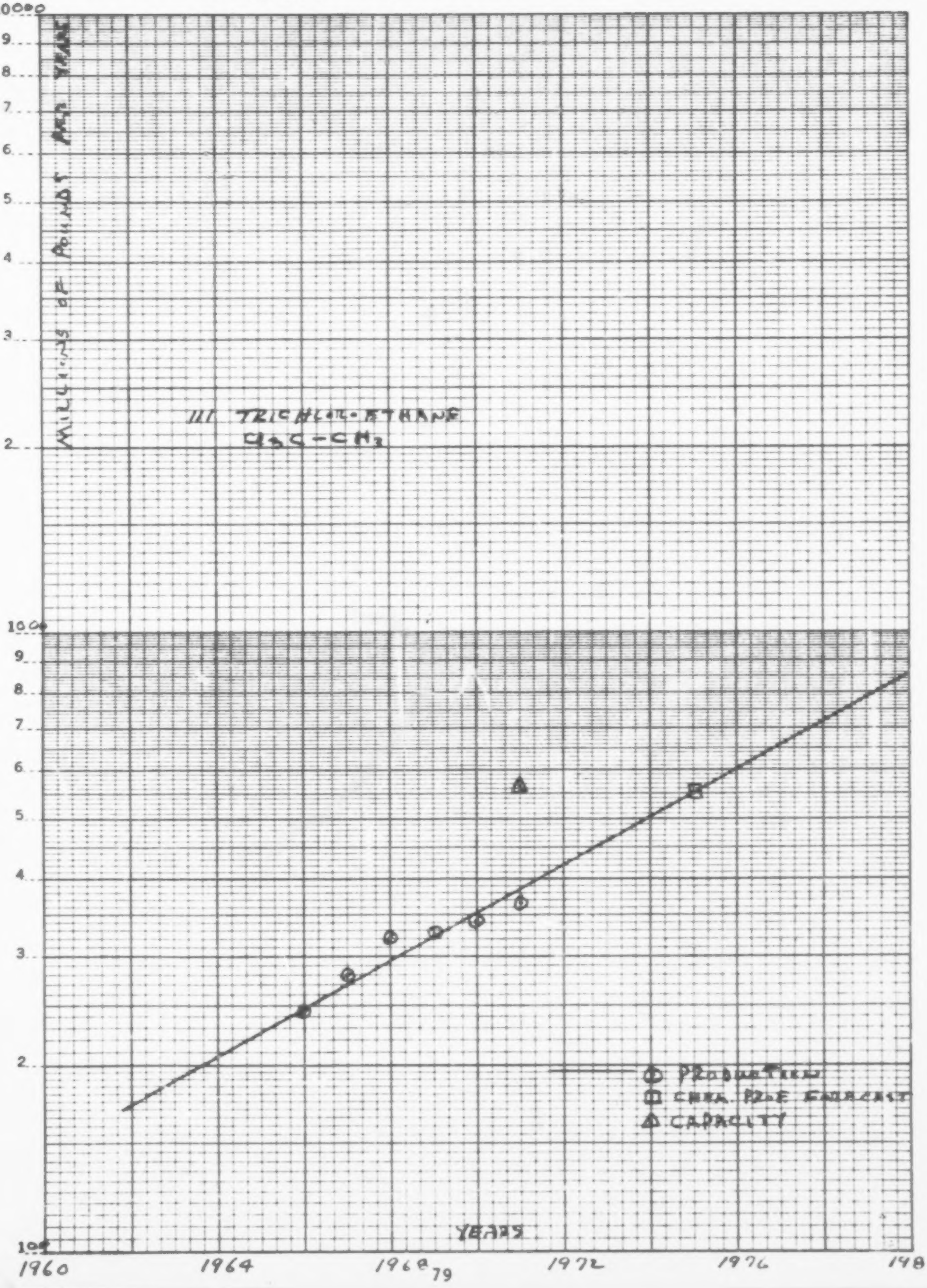
This reaction will be studied in this part of the report. In the second step, 1,1-dichloroethane is thermally chlorinated:

$$Cl_2 + C_2H_4Cl_2 \longrightarrow C_2H_3Cl_3 + HCl$$

which will also be studied here.

As indicated above, the main use of TCE is as a solvent.

CHART 7



K+E SEMI-LOGARITHMIC 46 4853
2 CYCLES X 80 DIVISIONS MADE IN U.S.A.
KEUFFEL & ESSER CO.

Process: Hydrochlorination, Then Chlorination of Vinyl Chloride

Recycled 1,1-dichloroethane (DCE) vapor and chlorine gas are fed to a tower-type reactor, at about 400C and atmospheric pressure, producing TCE and hydrogen chloride. Yields are over 95 percent. After cooling the reactor products to about 40C, they are mixed with fresh vinyl chloride (VC) and fed to a tower-type hydrochlorinator in which a liquid mixture of DCE and TCE, containing some ferric chloride catalyst, is recirculated. The hydrogen chloride reacts with the VC producing DCE. The hydrochlorinator is maintained at about 40C by cooling the recycled DCE/TCE mixture and at atmospheric pressure by venting the inerts. The hydrochlorinator products are decanted from the catalyst and fed to the purification-separation system. Yields are over 95 percent.

The purification-separation system consists of the following steps:

Adjustment of chlorination
Steam distillation
Decanting
Drying
DCE stripping
TCE fractionation

The chloride contents of the products from the hydrochlorinator are adjusted by a light chlorination. The products are then stripped from the heavies by steam distillation, decanted from the condensed steam, and dried. From the drier the products are fed to the first distillation column, where the DCE is stripped off and recycled. The first column bottoms are fed to the second distillation column, where the TCE is taken off overhead.

The raw materials are vinyl chloride, chlorine, ferric chloride, and dessicant. The by-products are chloroethanes and heavies.

There are two sources of air pollution. First, to keep inerts from building up in the hydrochlorinator, it is vented to the atmosphere. Second, there is a purge on the recycled DCE line, for inerts control.

PR 100

FLOWSHEET

Job EPA

Location CHLORINE STUDY

Subject 1,1,1- TRICHLORO ETHANE

PROCESSES RESEARCH, INC.

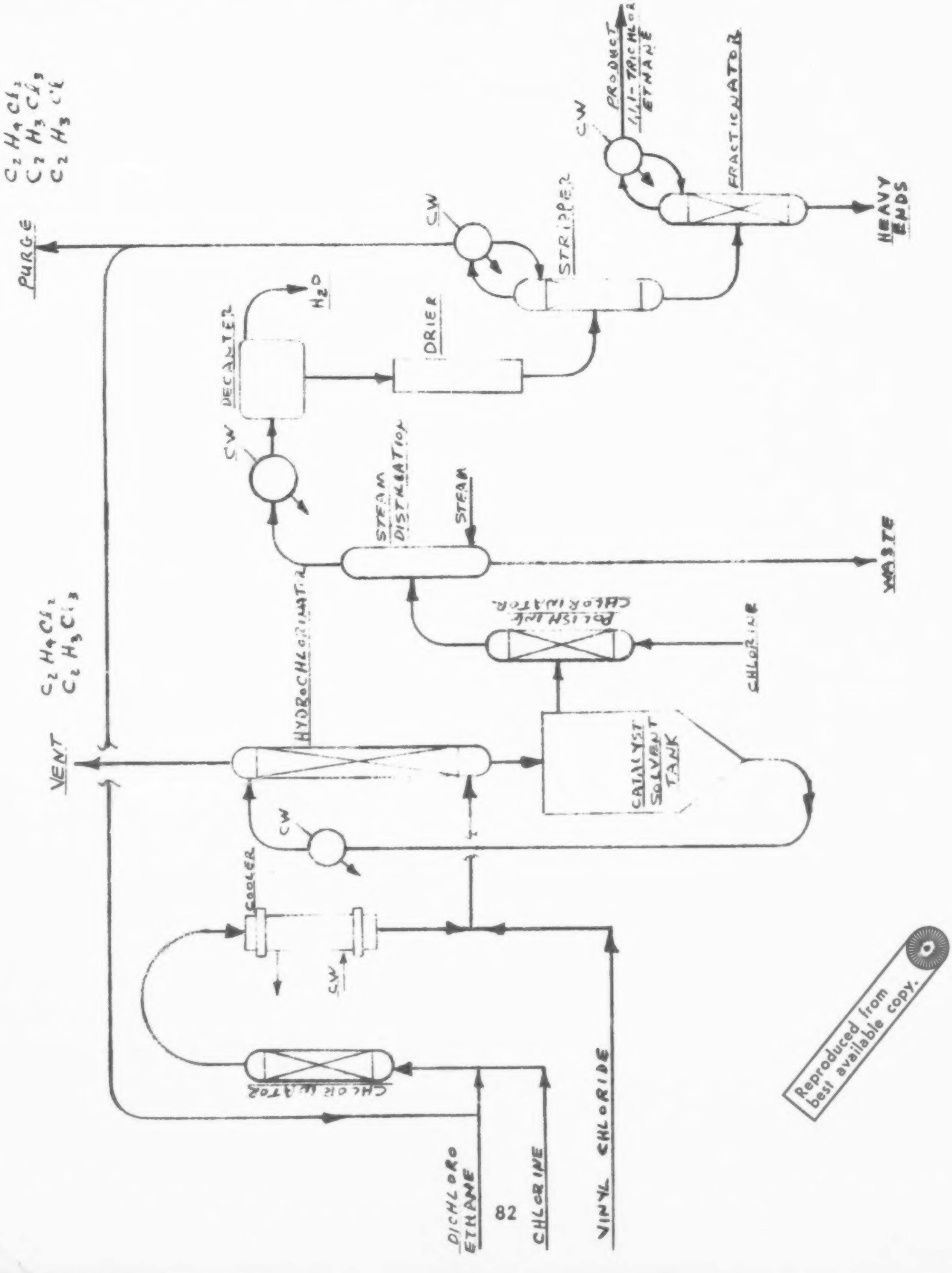
INDUSTRIAL PLANNING AND RESEARCH

CINCINNATI NEW YORK

File No 3393 Sheet No 1

Checked by ______ Date ______

Computed by SPK Date 11-4-7


PURGE
$C_2H_4Cl_2$
$C_2H_3Cl_3$
C_2H_3Cl
VENT
$C_2H_4Cl_2$
$C_2H_3Cl_3$
CW
STRIPPER
CW
FRACTIONATOR
PRODUCT 1,1,1-TRICHLOROETHANE
HEAVY ENDS
DECANTER
H_2O
DRIER
CW
STEAM DISTILLATION
STEAM
WASTE
HYDROCHLORINATOR
POLISHING CHLORINATOR
CHLORINE
CATALYST SOLVENT TANK
CW
COOLER
CW
CHLORINATOR
DICHLORO ETHANE
CHLORINE
VINYL CHLORIDE

PROCESS: HYDROCHLORINATION THEN CHLORINATION OF VINYL CHLORIDE.

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PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO. 2818	INDUSTRY IOC	PRODUCT 1,1,1-TRICHLORO-ETHANE, $C_2H_3Cl_3$
DATE: 10-27-71	PROCESS HYDROCHLORINATION AND CHLORINATION OF VINYL CHLORIDE	

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒	2	8	1	8	
PRODUCT : COLS. 5-8	☒		1	2	8	
PROCESS : COLS. 9-13				4	4	

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
38	DOW	FREEPORT, TX	A	300	A
53	ETHYL	BATON ROUGE, LA	A	40	A
53	PPG	LAKE CHARLES, LA	A	175	A
53	VULCAN	GEISMAR, LA	A	50	A

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 49	50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

1 of 2

INDUSTRY NO. 2818	INDUSTRY ICC	PRODUCT 1,1,1- TRICHLORO- ETHANE, $C_2H_3Cl_3$	
DATE PREPARED 10-27-71	PROCESS HYDROCHLORINATION THEN CHLORINATION OF VC	SOURCE STRIPPER	

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒	2	8	1	8
PRODUCT : COLS. 5-8	☒		1	2	8
PROCESS : COLS. 9-13				4	4
SOURCE : COLS. 14-17	☒			3	6

POLLUTANT			CONTROL DEVICE				
DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
$C\ H_4Cl_2$	1	C	NONE				
$C_2H_3Cl_3$	1	C	"				
C_2H_3Cl	1	C	"				

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23	UNCON EMISS 24 30	Q 31	CEF 32 36	Q 36	SCF 37 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ______

RELATED INDUSTRIES

BIBLIOGRAPHY

2-2

SOURCE DATA TABULATION

INDUSTRY NO. 2818	**INDUSTRY** IOC	**PRODUCT** 1,1,1- TRICHLOROETHANE, $C_2H_3Cl_3$	**COMPUTER CODE NOS.**
DATE PREPARED 10-27-71	**PROCESS** HYDROCHLORINATION THEN CHLORINATION OF VC	**SOURCE** HYDROCHLORINATOR	

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒	2	8	1	8
PRODUCT : COLS. 5-8	☒		1	2	8
PROCESS : COLS. 9-13				4	4
SOURCE : COLS. 14-17	☒			3	0

POLLUTANT			**CONTROL DEVICE**				
DESCRIPTION	**EMISSION FACTOR**	**Q**	**TYPE**	**EFF. FACTOR**	**Q**	**SOURCE FACTOR**	**Q**
$C_2H_4Cl_2$	17	c	None				
$C_2H_3Cl_3$	18	c	"				

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23	UNCON EMISS 24 30	Q 31	CEF 32 35	Q 36	SCF 37 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ______________________

RELATED INDUSTRIES

BIBLIOGRAPHY

Product: Allyl Chloride

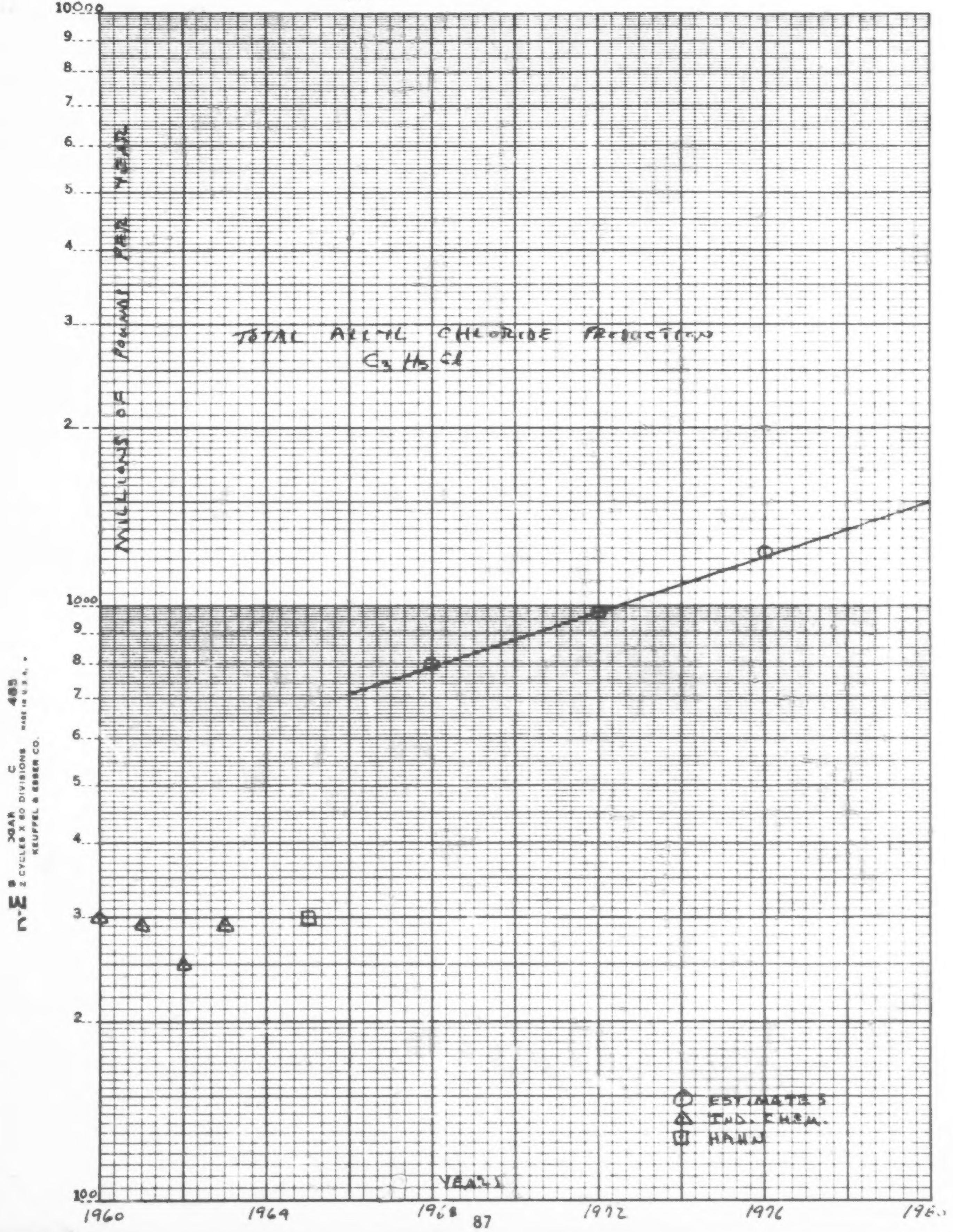
Allyl chloride is made by chlorinating propylene at high temperatures (400 to 500C). If lower temperatures (less than, say, 300C) are used, the reaction becomes an addition reaction, yielding dichloropropane. For allyl chloride, the equation is:

$$Cl_2 + C_3H_6 \xrightarrow{500C} C_3H_5Cl + HCl$$

The yields are about 85 percent.

Allyl chloride is an important intermediate. Glycerol, allyl alcohol, and epichlorohydrin are made from allyl chloride. Chart 9 shows an estimate of the production of allyl chloride from 1960 to 1970, with a projection to 1980. These data are based on synthetic glycerol, epoxy resins, epichlorohydrin production, and miscellaneous uses.

CHART 9


TOTAL ALLYL CHLORIDE PRODUCTION
C_3H_5Cl
MILLIONS OF POUNDS PER YEAR
YEARS
10000
9
8
7
6
5
4
3
2
1000
9
8
7
6
5
4
3
2
100
1960
1964
1968
1972
1976
1980
○ ESTIMATES
△ IND. CHEM.
□ HANN
K&E 2 CYCLES X 60 DIVISIONS
KEUFFEL & ESSER CO.
MADE IN U.S.A.
485

Process: Chlorination of Propylene

Industrial scale allyl chloride facilities perform three major processing operations: feed preparation, reaction, and product recovery.

Feed Preparation. The propylene is purified by fractionation and drying. The chlorine is also dried.

Reaction. The reaction is carried out in an adiabatic reactor designed to provide rapid and intimate mixing. Reaction temperature is controlled by balancing the mole ratio of the feed (usually 4 moles of propylene to one of chlorine) and propylene preheat temperature. The usual reaction temperature range is 500 to 510C; pressures of 15 pounds per square inch gage are used. Chlorine utilization is in excess of 99 percent. Reactor products are then cooled to about 50C.

Product Recovery. After initial removal of hydrogen chloride and propylene, the allyl chloride fraction is separated in a conventional two-step distillation. Yields of allyl chloride are about 85 percent.

The raw materials are chlorine (dry gas) and propylene (dry gas). The by-products are coke, dichloropropane, hydrogen chloride, and chloropropenol (mostly 2-chloropropene).

There is one air pollution source from the allyl chloride process, the purge on the propylene recycle circuit to remove inerts, mainly impurities in the raw materials. The noncondensables from the stripping column are vented into the suction of the recycle compressor.

FR 100

FLOWSHEET

Job EPA
Location CHLORINE STUDY
Subject ALLYL CHLORIDE

PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING
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CINCINNATI NEW YORK

File No 03383 Sheet No 1
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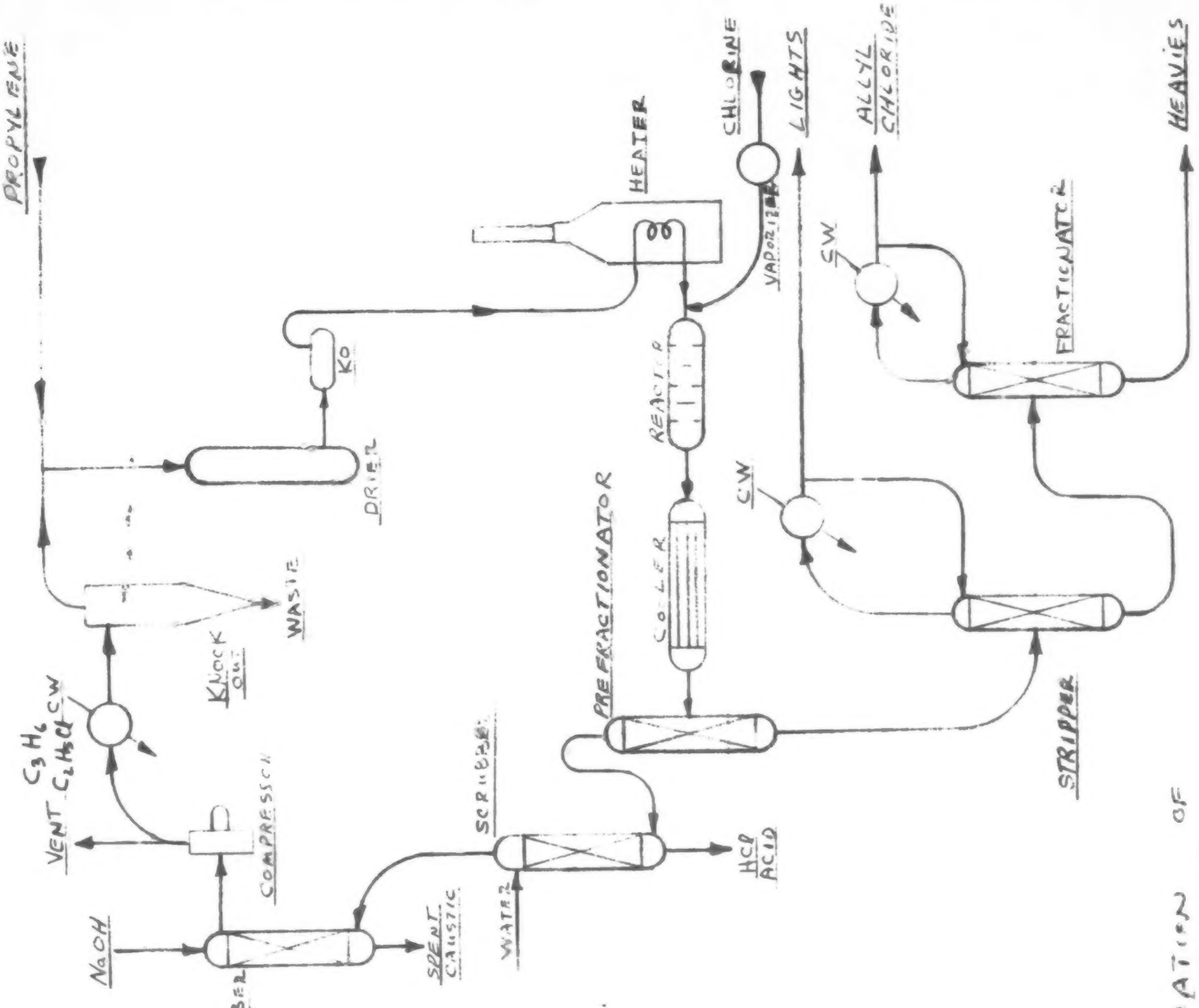

PROPYLENE
HEATER
CHLORINE
VAPORIZER
LIGHTS
ALLYL CHLORIDE
HEAVIES
CW
FRACTIONATOR
KO
REACTOR
DRIER
CW
COOLER
PREFRACTIONATOR
WASTE
KNOCK OUT
STRIPPER
C_3H_6
C_2H_5Cl
CW
VENT
COMPRESSOR
SCRUBBER
HCl ACID
NaOH
ABSORBER
SPENT CAUSTIC
WATER

PROCESS: CHLORINATION OF
PROPYLENE

PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO. 2818	INDUSTRY IOC	PRODUCT ALLY CHLORIDE C_3H_5Cl
DATE: 10-27-71	PROCESS CHLORINATION OF PROPYLENE	

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒	2	8	1	8	
PRODUCT : COLS. 5-8	☒		1	3	2	
PROCESS : COLS. 9-13				4	8	

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
15	ATLAS	WILMINGTON, DE	C	150	C
38	DOW	FREEPORT, TX	B	195	B
193	OLIN	BRANDENBURG, KY	B	40	B
38	SHELL	DEER PARK, TX	B	215	B
53	SHELL	NORCO, LA	B	50	C
UNCL	CIBA	TOMS RIVER, NJ	B	34	B

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 49	50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO. 2818	**INDUSTRY** IOC	**PRODUCT** ALLYL CHLORIDE C_3H_5Cl	**COMPUTER CODE NOS.**					
			SIC. NO. : COLS. 1-4	☒	2	8	1	8
			PRODUCT : COLS. 5-8	☒		1	3	2
DATE PREPARED 10-27-71	**PROCESS** CHLORINATION OF PROPYLENE	**SOURCE** ABSORBER	**PROCESS : COLS. 9-13**				4	8
			SOURCE : COLS. 14-17	☒			4	3

POLLUTANT — CONTROL DEVICE

DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
C_3H_6	27	C	NONE				
C_2H_5Cl	27	C	"				

COMPUTER CODE NOS.

PNO 18-20	CNO 21-23	UNCON EMISS 24-30	Q 31	CEF 32-35	Q 36	SCF 37-40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ______________________

RELATED INDUSTRIES

BIBLIOGRAPHY

Product: Chloroform

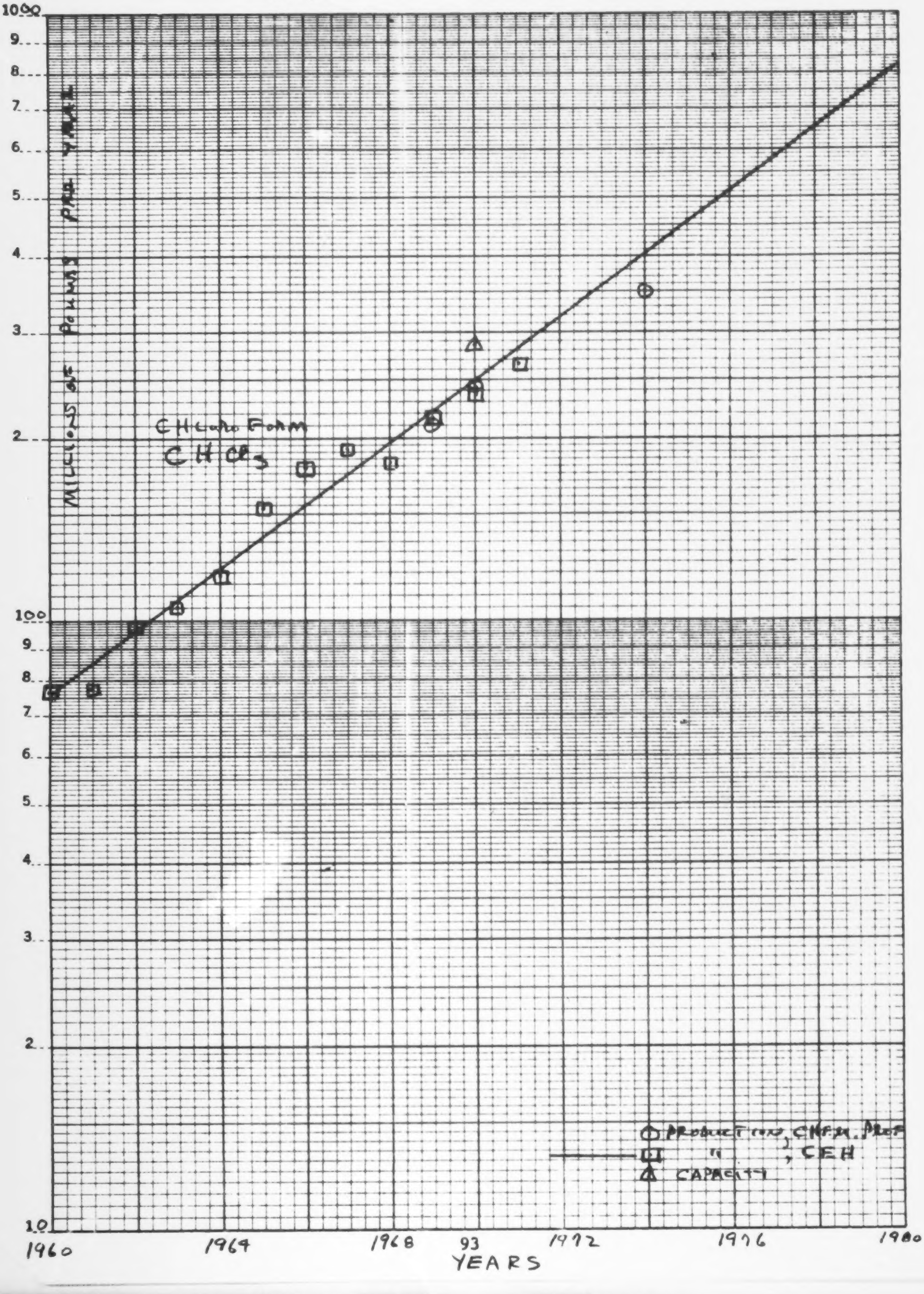
Chloroform is a co-product from the chlorination of methane, along with methyl chloride, methylene chloride, and carbon tetrachloride. The reaction is:

$$CH_4 + 3Cl_2 \longrightarrow CHCl_3 + 3HCl$$

Chart 10 shows the production and capacity figures for chloroform. The production growth rate for the past ten years has been 12 percent per year. A production rate of 800 million pounds per year is expected in 1980.

The main use (52 percent) of chloroform is as an intermediate for making Freon-22, monochlorodifluoromethane.

CHART 10


1000
9.
8.
7.
6.
5.
4.
3.
2.
100.
9.
8.
7.
6.
5.
4.
3.
2.
1.0
MILLIONS OF POUNDS PER YEAR
CHLOROFORM
$CHCl_3$
PRODUCTION, CHEM. PROF
" , CEH
CAPACITY
1960
1964
1968
93
1972
1976
1980
YEARS

Process: Chlorination of Methane

The process sequence requires four main steps: (1) reaction, (2) HCl recovery, (3) chlorides recovery, and (4) chlorides refining. High-purity methane, chlorine, and recycle methane are premixed and fed to the reactor. The reactor effluent, containing organic chlorides, HCl, excess methane, and only traces of chlorine, is cooled and fed to the HCl recovery system. The first column in this system is an absorber designed for efficient HCl removal. The bulk of the absorbing liquor is HCl azeotrope (about 20 percent by weight HCl). The rich acid is thus above the azeotrope and allows stripping of anhydrous HCl. The second column distills off anhydrous HCl and produces the required azeotrope in the bottoms. For high yields of chloroform, the amount of recirculating methane is reduced. Temperature and pressures have little effect. Equipment design does have effect and is important.

The HCl-free gases from the absorber are washed with caustic soda to remove final traces of HCl and are then ready for chlorides recovery. For the intermediate product distribution under discussion, compression, cooling, and drying with sulfuric acid are an economical combination.

The reactor is operated at 15 pounds per square inch gage and 400 to 500C. The yields are over 95 percent. There is one source of air pollution. It is a purge on the recycled methane to remove inerts. The vents from the product purification system are returned to the suction side of the recycle compressor.

The raw materials are chlorine (dry gas), methane (99 percent plus), sulfuric acid, and caustic soda. The by-products are other chloromethanes, perchloroethylene, hydrogen chloride, heavy ends, and spent caustic sludge.

FR 109

FLOWSHEET

Job EPA

Location CHLORINE STUDY

Subject CHLORIDES OF METHANE

PROCESSES RESEARCH, INC.

INDUSTRIAL PLANNING
AND RESEARCH

CINCINNATI NEW YORK

File No. 03383 Sheet No 1

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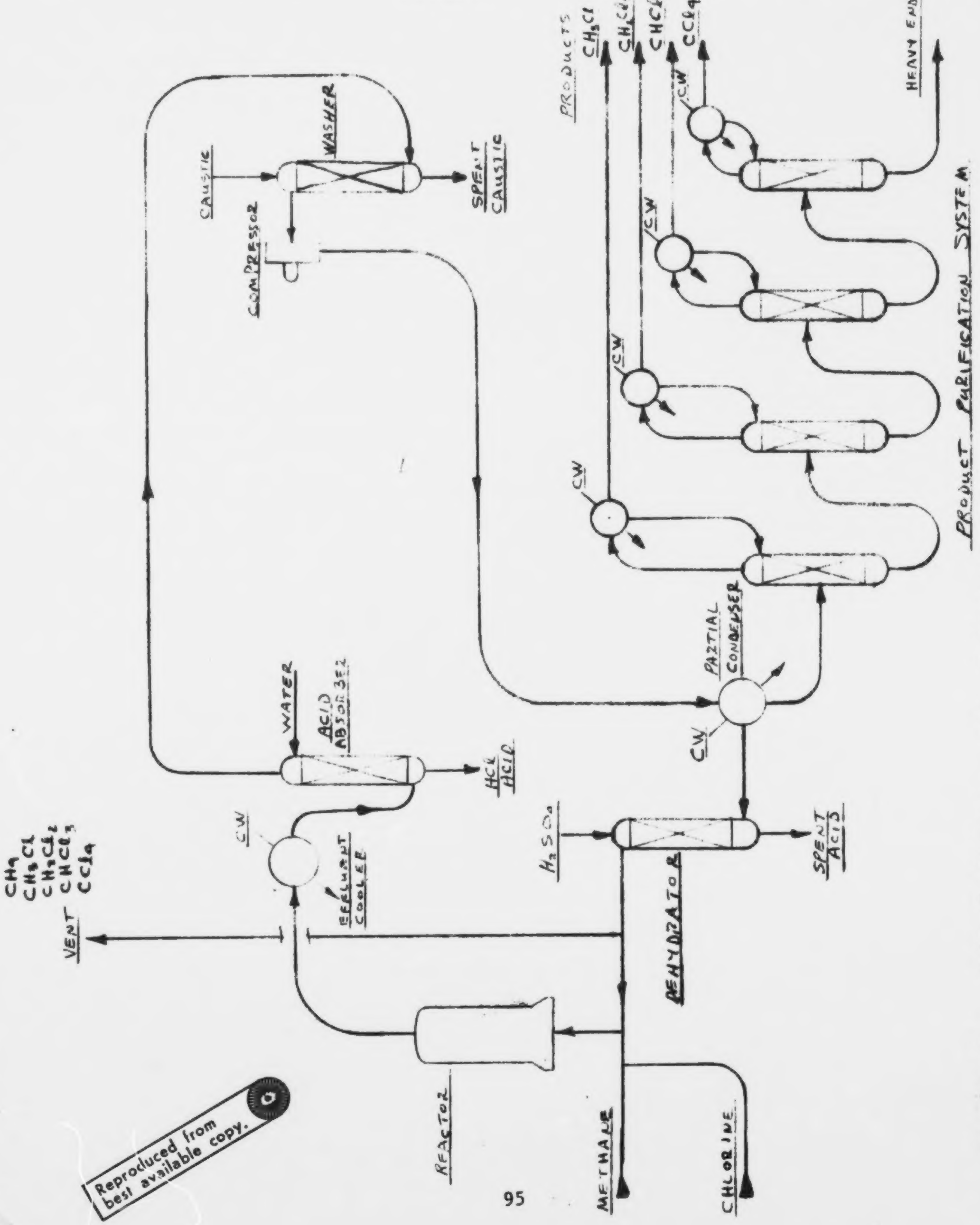
PRODUCTS
CH3Cl
CH2Cl2
CHCl3
CCl4
HEAVY ENDS
CW
CW
CW
CW
PRODUCT PURIFICATION SYSTEM
WASHER
CAUSTIC
SPENT CAUSTIC
COMPRESSOR
PARTIAL CONDENSER
CW
WATER
ACID ABSORBER
HCl ACID
CW
EFFLUENT COOLER
CH4
CH3Cl
CH2Cl2
CHCl3
CCl4
VENT
H2SO4
DEHYDRATOR
SPENT ACID
REACTOR
METHANE
CHLORINE

PROCESS: CHLORINATION OF METHANE

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PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO.	INDUSTRY	PRODUCT
2818	IOC	CHLOROFORM $CHCl_3$
DATE:	**PROCESS**	
10-28-71	CHLORINATION OF METHANE	

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒	2	8	1	8	
PRODUCT : COLS. 5-8	☒		1	1	1	
PROCESS : COLS. 9-13				3	2	

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
33	ALLIED	MOUNDSVILLE, WV	A	30	A
10	DIAMOND	BELLE, WV	C	15	C
39	DOW	FREEPORT, TX	A	100	A
53	DOW	PLAQUEMINE, LA	A	30	A
2[illegible]	DUPONT	NIAGARA FALLS, NY	A	15	A
3[illegible]	STAUFFER	LOUISVILLE, KY	A	75	A
12	VULCAN	NEWARK, NJ	A	10	A
2[illegible]	VULCAN	WICHITA, KS	A	10	A

COMPUTER CODE NOS.

AQCR 19–22	STATE 23 24	CITY 25–36	COMPANY 37–49	50 51	CAPACITY 52–55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO. 2818	**INDUSTRY** IOC	**PRODUCT** CHLOROFORM $CHCl_3$	**COMPUTER CODE NOS.**
DATE PREPARED 10-28-71	**PROCESS** CHLORINATION OF METHANE	**SOURCE** DEHYDRATOR	

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒	2	8	1	8
PRODUCT : COLS. 5-8	☒		1	1	7
PROCESS : COLS. 9-13				3	3
SOURCE : COLS. 14-17	☒			4	3

POLLUTANT / CONTROL DEVICE

DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
CH_4	2	C	NONE				
CH_3Cl	26	C	"				
CH_2Cl_2	4	C	"				
$CHCl_3$	2	C	"				
$-CCl_4$	2	C	"				

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23	UNCON EMISS 24 30	Q 31	CEF 32	Q	SCF 37 40	Q 41	YR 42	DATE ISS.	REV.NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ____________

RELATED INDUSTRIES

BIBLIOGRAPHY

Product: Methyl Chloride

In 1970, over 70 percent of the methyl chloride was made by chlorinating methane:

$$Cl + CH_4 \longrightarrow CH_3Cl + HCl$$

An older process, using methanol and hydrogen chloride, produced about 22 percent of the methyl chloride in 1970. The reaction is:

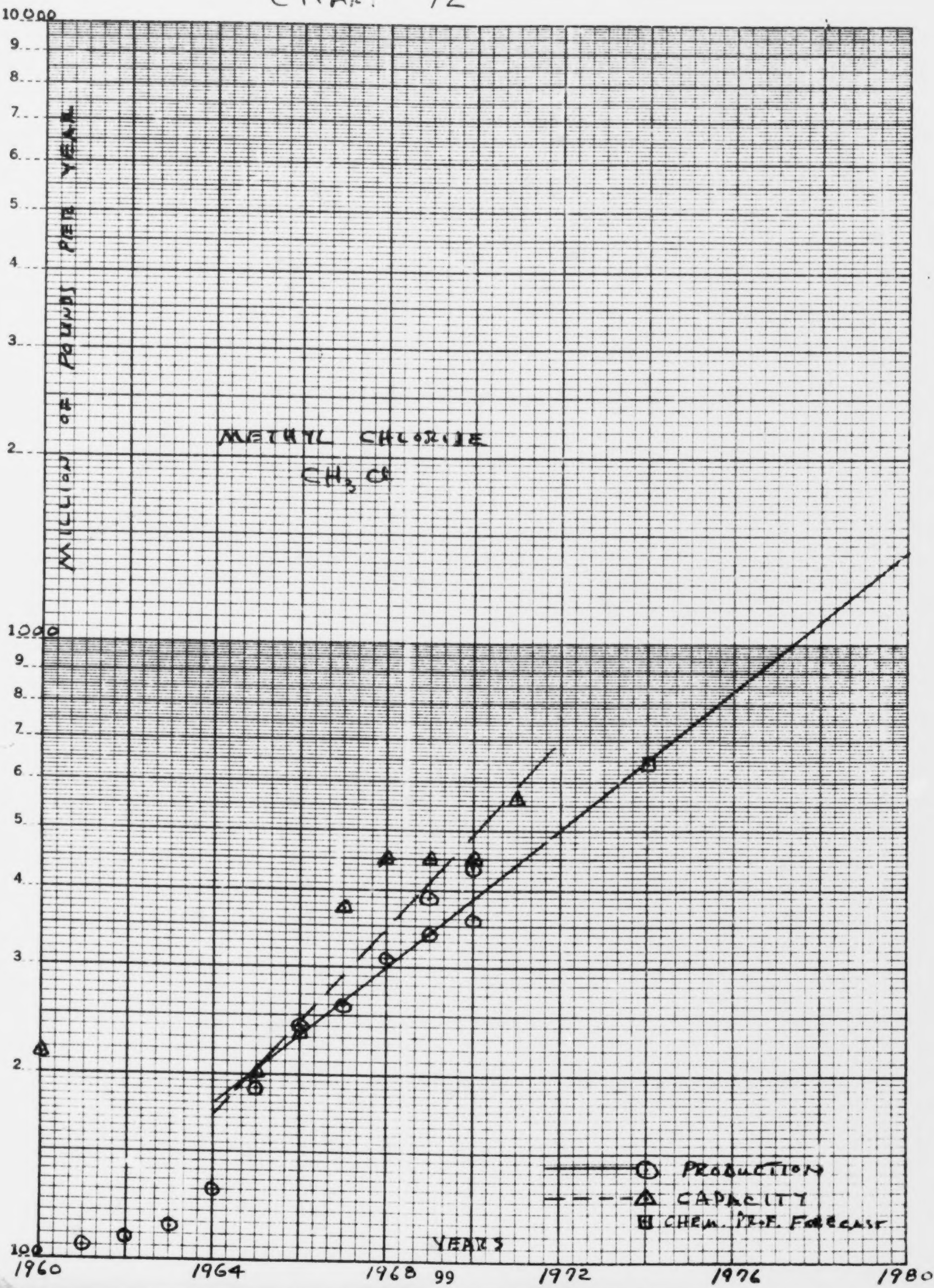
$$CH_3OH + HCl \longrightarrow CH_3Cl + H_2O$$

In 1960 this reaction produced about 77 percent of the methyl chloride.

Chart 12 shows the production and capacity data of methyl chloride. For the past ten years the annual growth rate has been 19 percent. For the future, the growth is expected to be at about half this rate.

The main uses of methyl chloride are as an intermediate for producing silicones and tetramethyl lead.

CHART 12


10,000
9
8
7
6
5
4
3
2
MILLION OF POUNDS PER YEAR
METHYL CHLORIDE
CH_3Cl
1000
9
8
7
6
5
4
3
2
100
1960
1964
1968
99
1972
1976
1980
YEARS
PRODUCTION
CAPACITY
CHEM. PROF. FORECAST
2 CYCLES X 60 DIVISIONS
KEUFFEL & ESSER CO

Process: Chlorination of Methane

The process sequence requires four main steps: (1) reaction, (2) HCl recovery, (3) chlorides recovery, and (4) chlorides refining. High-purity methane, chlorine, and recycle methane are premixed and fed to the reactor. The reactor effluent, containing organic chlorides, HCl, excess methane, and only traces of chlorine, is cooled and fed to the HCl recovery system. The first column in this system is an absorber designed for efficient HCl removal. The bulk of the absorbing liquor is HCl azeotrope (about 20 percent by weight HCl). The rich acid is thus above the azeotrope and allows stripping of anhydrous HCl. The second column distills off anhydrous HCl and produces the required azeotrope in the bottoms. For high yields of methyl chloride, the amount of recirculating methane is increased.

The HCl-free gases from the absorber are washed with caustic soda to remove final traces of HCl and are then ready for chlorides recovery. For the intermediate product distribution under discussion, compression, cooling, and drying with sulfuric acid are an economical combination.

The reactor is operated at 15 pounds per square inch gage and 400 to 500C. The yields are over 95 percent. There is one source of air pollution. It is a purge on the recycled methane to remove inerts. The vents from the product purification system are returned to the suction side of the recycle compressor.

The raw materials are chlorine (dry gas), methane (99 percent plus), sulfuric acid, and caustic soda. The by-products are other chloromethanes, perchloroethylene, hydrogen chloride, heavy ends, and spent caustic sludge.

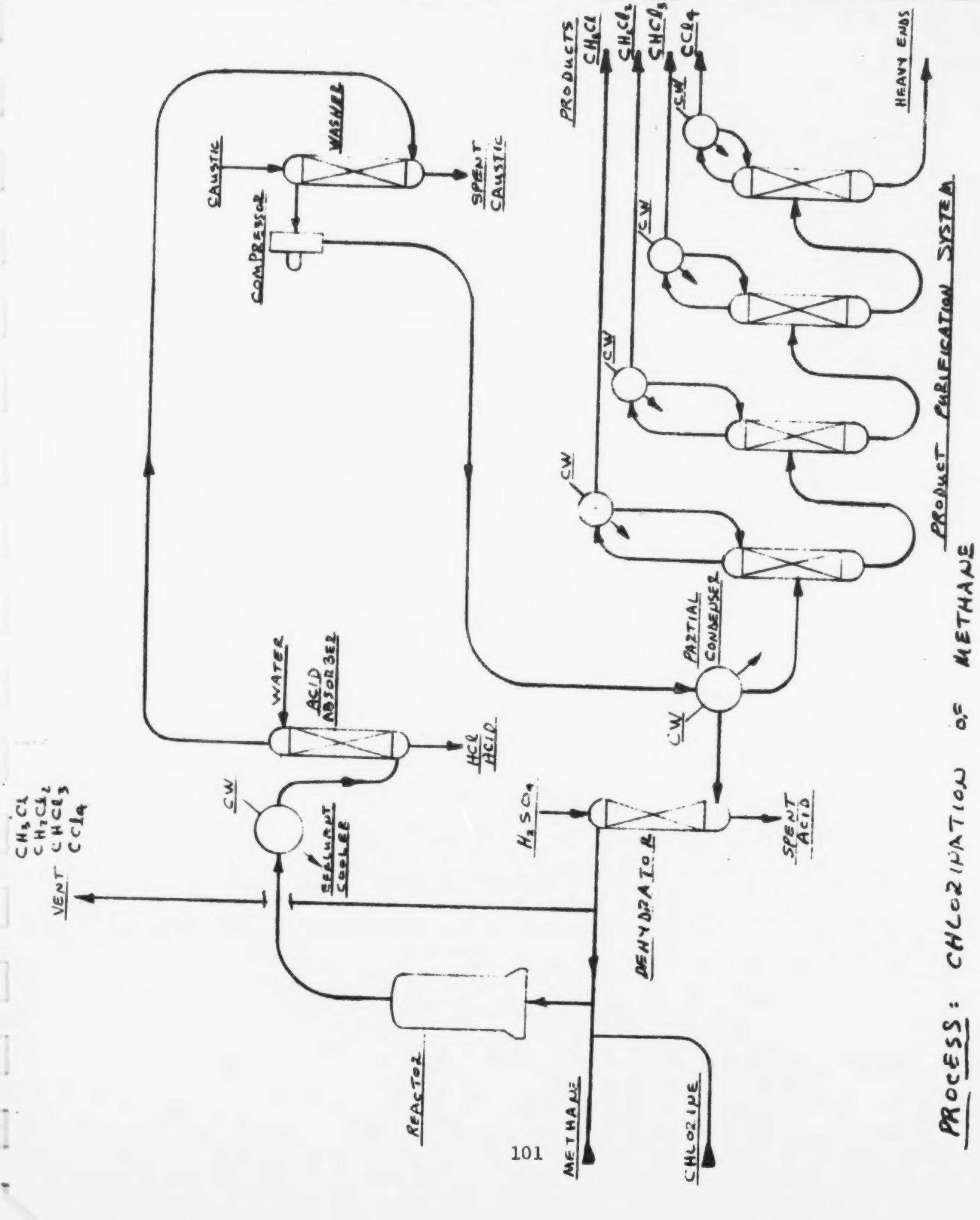
PR 109

FLOWSHEET

PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING
AND RESEARCH
CINCINNATI NEW YORK

Job EPA
Location CHLORINE STUDY
Subject CHLORIDES OF METHANE

File No. 03383 Sheet No. 1
Checked by ______ Date ______
Computed by SPK Date 11-3-71


PRODUCTS
CH_3Cl
CH_2Cl_2
$CHCl_3$
CCl_4
HEAVY ENDS
CW
CW
CW
CW
PRODUCT PURIFICATION SYSTEM
CAUSTIC
WASHER
SPENT CAUSTIC
COMPRESSOR
PARTIAL CONDENSER
CW
WATER
ACID ABSORBER
HCl ACID
CW
EFFLUENT COOLER
CH_3Cl
CH_2Cl_2
$CHCl_3$
CCl_4
VENT
H_2SO_4
DEHYDRATOR
SPENT ACID
REACTOR
METHANE
CHLORINE

PROCESS: CHLORINATION OF METHANE

PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO. 2818	INDUSTRY IOC	PRODUCT METHYL CHLORIDE CH_3Cl
DATE: 10 20 [illegible]	PROCESS CHLORINATION OF METHANE	

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒	2	8	1	8	
PRODUCT : COLS. 5-8	☒		1	2	3	
PROCESS : COLS. 9-13				3	3	

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
33	ALLIED	MOUNDSVILLE, WV	A	25	B
38	DOW	FREEPORT, TX	A	70	B
20	DOW-CORNING	CARROLLTON, KY	B	20	B
53	DOW	PLAQUEMINE, LA	A	71	B
233	UNION CARBIDE	INSTITUTE, WV	A	24	B
21	DOW	PITTSBURG, CA	A	25	B
24	DUPONT	NIAGARA FALLS, NY	A	80	B
35	STAUFFER	LOUISVILLE, KY	A	15	B

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 49	50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

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SOURCE DATA TABULATION

INDUSTRY NO. 2818	**INDUSTRY** IOC	**PRODUCT** METHYL CHLORIDE CH_3Cl	
DATE PREPARED 10-28-71	**PROCESS** CHLORINATION OF METHANE	**SOURCE** DEHYDRATOR	

COMPUTER CODE NOS.

SIC. NO. :	COLS. 1-4	☒	2	8	1	8
PRODUCT :	COLS. 5-8	☒		1	2	3
PROCESS :	COLS. 9-13				3	3
SOURCE :	COLS. 14-17	☒			4	3

POLLUTANT / CONTROL DEVICE

DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
CH_4	2	C	NONE				
CH_3Cl	26	C	"				
CH_2Cl_2	4	C	"				
$CHCl_3$	2	C	"				
CCl_4	2	C	"				

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23	UNCON EMISS 24 30	Q 31	CEF 32 35	Q 36	SCF 37 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ____________

RELATED INDUSTRIES

BIBLIOGRAPHY

Process: Hydrochlorination of Methanol

Methyl chloride is produced by the action of hydrogen chloride on methanol, with the aid of a catalyst, in the vapor phase.

Vapors of methanol and hydrogen chloride are continuously mixed in approximately equimolecular ratios and passed through a preheater maintained at about 180C. The gas mixture is then passed at substantially atmospheric pressure through a converter at a temperature of 340 to 350C. The converter is packed with previously ignited alumina gel of 8- to 12-mesh size or a similar acting catalyst, such as zinc chloride on pumice, cuprous chloride, or activated carbon. The converter is externally heated by electric coils or some other suitable means. Space velocities of about 275 cubic feet per hour per cubic foot of gross catalyst volume are generally used (based on gas volumes at STP).

The effluent gases from the reactor are scrubbed with water to remove excess HCl, and alkali wash, and a strong sulfuric acid wash (to dry the product). Crude methyl chloride is distilled under pressure and at minus 24C to yield pure methyl chloride. The raw materials are 95 percent methanol, hydrogen chloride, and catalyst along with caustic and sulfuric acid. The by-products are heavies and excess HCl absorbed in water. There are no air pollution sources.

PR 109

FLOW SHEET

Job E.PA

Location CHLORINE STUDY

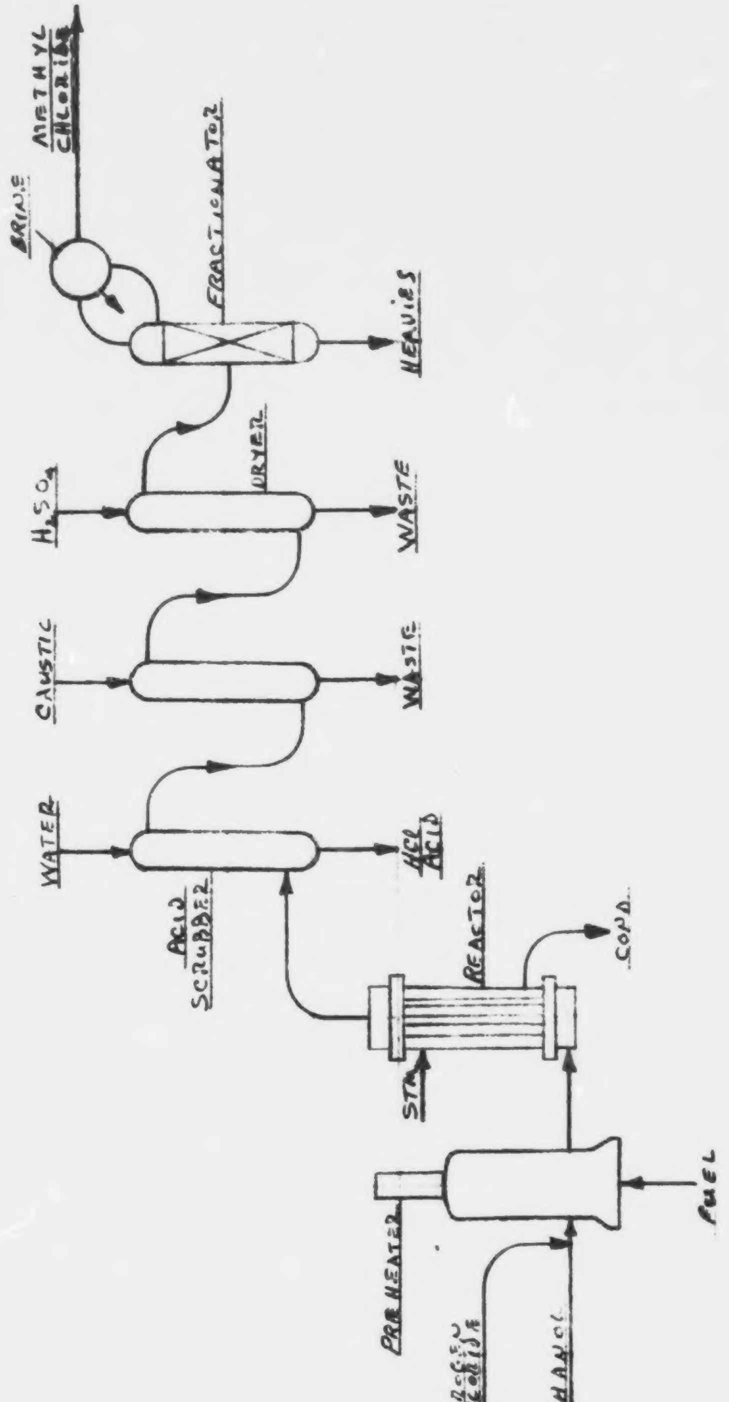
Subject METHYL CHLORIDE

PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING
AND RESEARCH
CINCINNATI NEW YORK

File No. 3383 Sheet No. 1

Charted by ______ Date ______

Computed by SPK Date 11-23-71


METHYL CHLORIDE
BRINE
FRACTIONATOR
HEAVIES
DRYER
H_2SO_4
WASTE
CAUSTIC
WASTE
WATER
HCl ACID
ACID SCRUBBER
REACTOR
COND.
STM
PREHEATER
FUEL
HYDROGEN CHLORIDE
METHANOL

PROCESS: HYDROCHLORINATION OF METHANOL

PROCESS DATA TABULATION

SH____OF____

SIC. NO.	INDUSTRY	PRODUCT
2818	IOC	METHYL CHLORIDE

DATE:	PROCESS
11-20-71	HYDROCHLORINATION OF METHANOL

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒	2	8	1	8	
PRODUCT : COLS. 5-8	☒		1	2	3	
PROCESS : COLS. 9-13				5	1	

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
53	ANCON	LAKE CHARLES, LA	A	100	B
195	DOW CORNING	MIDLAND, MI	A	15	B
53	ETHYL	BATON ROUGE, LA	A	75	B
48	GENERAL ELECTRIC	WATERFORD, NY	A	20	B
13	VULCAN	NEWARK, NJ	A	2	B

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 49	50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

Product: Methylene Chloride

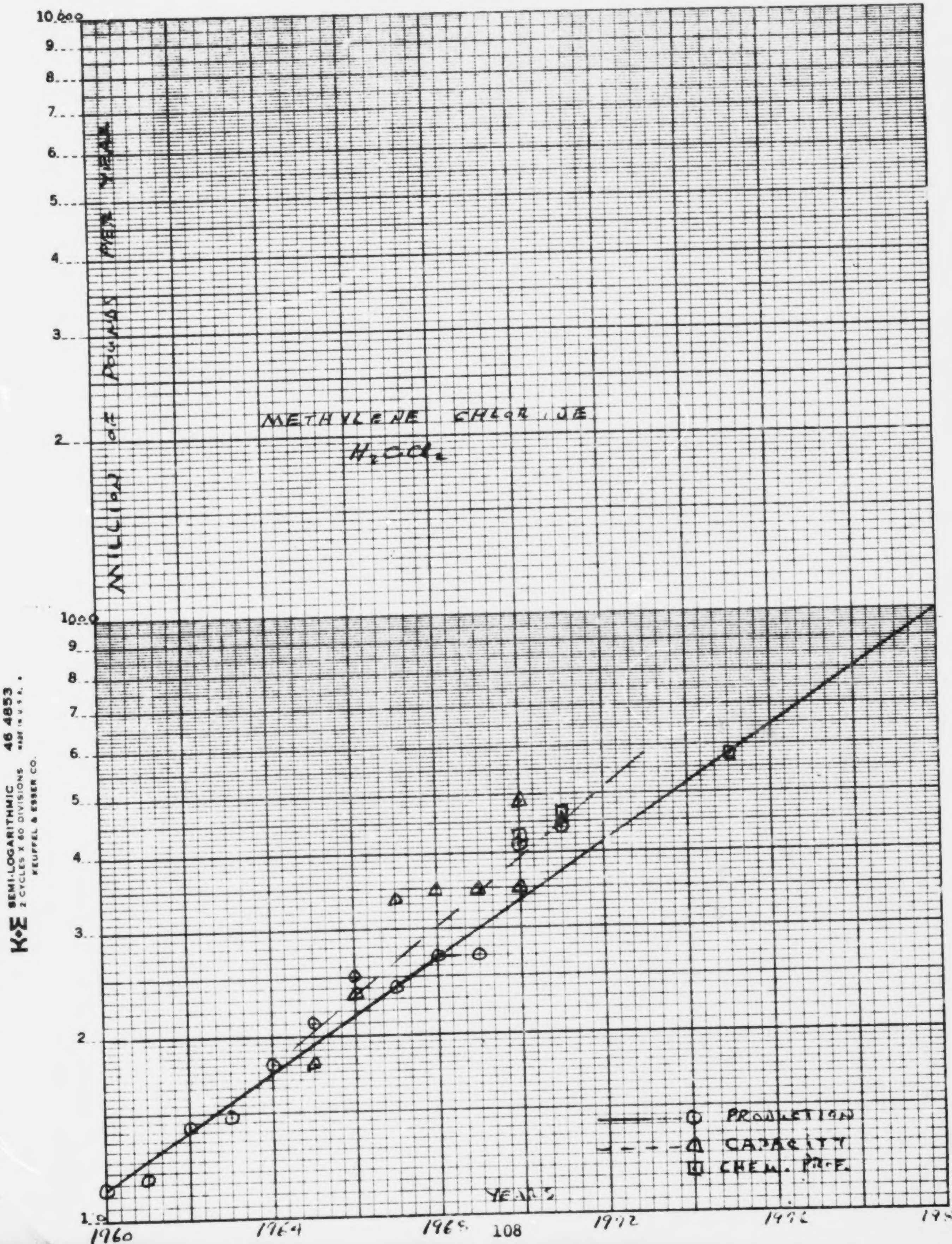
Methylene chloride is made by chlorinating methane:

$$2Cl_2 + CH_4 \longrightarrow CH_2Cl_2 + 2HCl$$

Its annual growth rate in the sixties was 14 percent. For the seventies, the growth rate is expected to decline to about half this rate, or about 7 percent. Chart 13 shows the production and capacity data.

The main use of methylene chloride, about 40 percent, is as a paint remover.

CHART 13


10,000
9
8
7
6
5
4
3
2
1000
9
8
7
6
5
4
3
2
1.0
MILLION of POUNDS PER YEAR
METHYLENE CHLORIDE
H_2CCl_2
PRODUCTION
CAPACITY
CHEM. PROF.
YEARS
1960
1964
1968
1972
1976
1980
K+E SEMI-LOGARITHMIC 46 4853
2 CYCLES X 60 DIVISIONS MADE IN U.S.A.
KEUFFEL & ESSER CO.

Process: Chlorination of Methane

The process sequence requires four main steps: (1) reaction, (2) HCl recovery, (3) chlorides recovery, and (4) chlorides refining. High-purity methane, chlorine, and recycled methane are premixed and fed to the reactor. The reactor effluent, containing organic chlorides, HCl, excess methane, and only traces of chlorine, is cooled and fed to the HCl recovery system. The first column in this system is an absorber designed for efficient HCl removal. The bulk of the absorbing liquor is HCl azeotrope (about 20 percent by weight HCl). The rich acid is thus above the azeotrope and allows stripping of anhydrous HCl. The second column distills off anhydrous HCl and produces the required azeotrope in the bottoms.

The HCl-free gases from the absorber are washed with caustic soda to remove final traces of HCl and are then ready for chlorides recovery. For the intermediate product distribution under discussion, compression, cooling, and drying with sulfuric acid are an economical combination.

The reactor is operated at 15 pounds per square inch gage and 400 to 500C. The yields are over 95 percent. There is one source of air pollution. It is a purge on the recycled methane to remove inerts. The vents from the product purification system are returned to the suction side of the recycle compressor.

The raw materials are chlorine (dry gas), methane (99 percent plus), sulfuric acid, and caustic soda. The by-products are other chloromethanes, perchloroethylene, hydrogen chloride, heavy ends, and spent caustic sludge.

PR 109

FLOWSHEET

Job EPA

Location CHLORINE STUDY

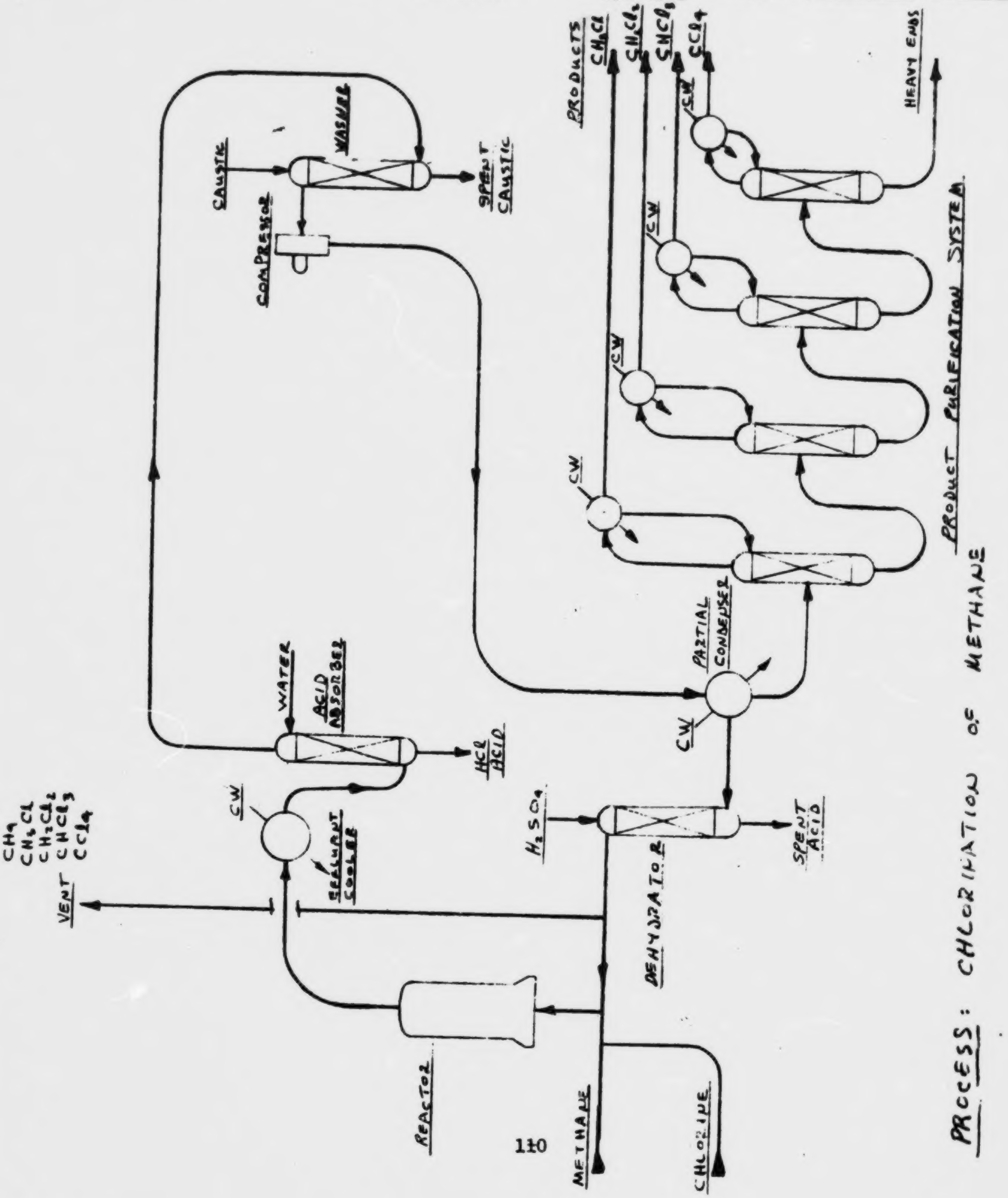
Subject CHLORIDES OF METHANE

PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING
AND RESEARCH
CINCINNATI NEW YORK

File No. 03383 Sheet No 1

Checked by ______ Date ______

Computed by SPK Date 11-3-71


PRODUCTS
CH_3Cl
CH_2Cl_2
$CHCl_3$
CCl_4
HEAVY ENDS
CW
WASHER
CAUSTIC
SPENT CAUSTIC
COMPRESSOR
CW
CW
CW
PRODUCT PURIFICATION SYSTEM
PARTIAL CONDENSER
CW
WATER
ACID ABSORBER
HCl ACID
CW
EFFLUENT COOLER
H_2SO_4
DEHYDRATOR
SPENT ACID
CH_3Cl
CH_2Cl_2
$CHCl_3$
CCl_4
VENT
REACTOR
METHANE
CHLORINE
PROCESS: CHLORINATION OF METHANE

PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO.	INDUSTRY	PRODUCT
2818	IOC	METHYLENE CHLORIDE, CH_2Cl_2

DATE:	PROCESS
10-29-71	CHLORINATION OF METHANE

COMPUTER CODE NOS.

SIC. NO.	: COLS. 1-4	☒	2	8	1	8
PRODUCT	: COLS. 5-8	☒		1	2	4
PROCESS	: COLS. 9-13				3	3

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
33	ALLIED	MOUNDSVILL, WV	A	50	B
70	DIAMOND	BELLE, WV	A	60	B
38	DOW	FREEPORT, TX	A	150	B
53	DOW	PLAQUEMINE, LA	A	60	B
24	DUPONT	NIAGARA FALLS, NY	A	40	B
35	STAUFFER	LOUISVILLE, KY	A	60	B
13	VULCAN	NEWARK, NJ	A	40	B
253	VULCAN	WICHITA, KS	A	30	B

COMPUTED CODE NOS.

AQCR 19-22	STATE 23-24	CITY 25-36	COMPANY 37-49	50-51	CAPACITY 52-55	Q 56	YEAR 57-58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO. 2818	**INDUSTRY** IOC	**PRODUCT** METHYLENE CHLORIDE, CH_2Cl_2	
DATE PREPARED 10-29-71	**PROCESS** CHLORINATION OF METHANE	**SOURCE** DEHYDRATOR	

COMPUTER CODE NOS.

SIC. NO. :	COLS. 1-4	☒	2	8	1	8
PRODUCT :	COLS 5-8	☒		1	2	4
PROCESS :	COLS. 9-13				3	3
SOURCE :	COLS. 14-17	☒			4	3

POLLUTANT			CONTROL DEVICE				
DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
CH_4	2	C	NONE				
CH_3Cl	26	C	"				
CH_2Cl_2	4	C	"				
$CHCl_3$	2	C	"				
CCl_4	2	C	"				

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23	UNCON EMISS 24 30	Q 31	CEF 32 35	Q 36	SCF 37 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ______

RELATED INDUSTRIES

BIBLIOGRAPHY

Product: Phosgene

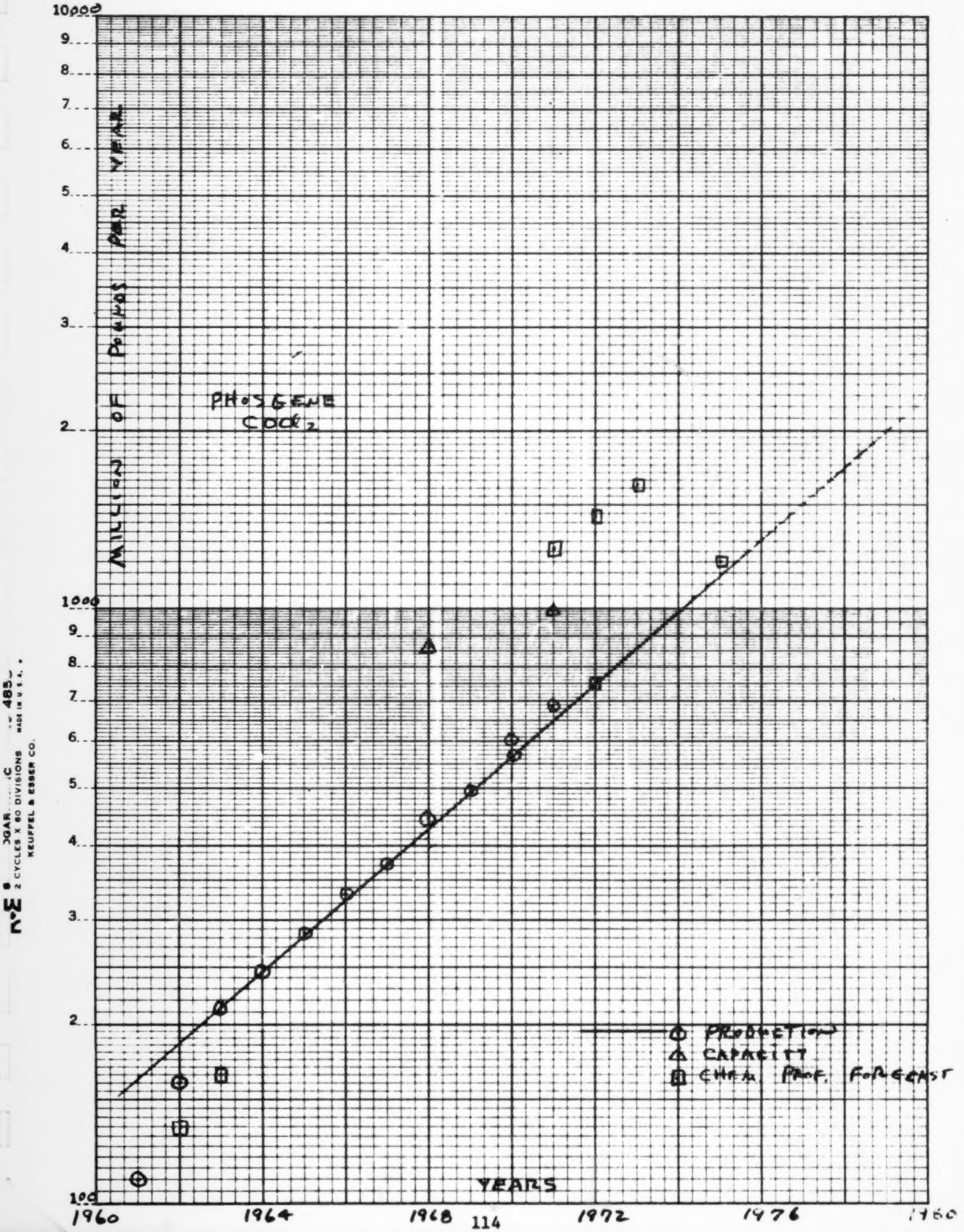
Phosgene is made by reacting chlorine and carbon monoxide:

$$Cl_2 + CO \longrightarrow COCl_2$$

Phosgene is very toxic, and was used as a poisonous gas in World War I. However, it is an excellent intermediate, especially for isocyanate production. Chart 14 shows the production and capacity data. In the sixties it had annual growth rate of 26 percent. For the seventies, an annual growth rate of 15 percent is forecast.

Its main use (62 percent) is as an intermediate for making tolylene di-isocyanate.

CHART 14


10000
9
8
7
6
5
4
3
2
1000
9
8
7
6
5
4
3
2
100
MILLION OF POUNDS PER YEAR
PHOSGENE
$COCl_2$
PRODUCTION
CAPACITY
CHEM. PROF. FORECAST
YEARS
1960
1964
1968
1972
1976
1980
K+E 2 CYCLES X 60 DIVISIONS KEUFFEL & ESSER CO. MADE IN U.S.A.

Process: Chlorination of Carbon Monoxide

Carbon monoxide and chlorine gases are dried, filtered, metered, and mixed, and then fed to a reactor with a very slight excess of CO. The reactor consists of water-cooled iron tubes filled with activated charcoal. Reactor conditions are 200C and 2 to 4 pounds per square inch gage. The reaction is highly exothermic. The hot gases from the reactor are cooled to about 0-C, and liquid phosgene condenses out. The noncondensables are scrubbed with benzene or toluene to remove the last traces of phosgene, and are vented. Yields are 99 percent.

The raw materials are carbon monoxide (dry), chlorine (dry), and activated charcoal. There are no by-products.

There is only one source of air pollutants, the noncondensables from the solvent absorber.

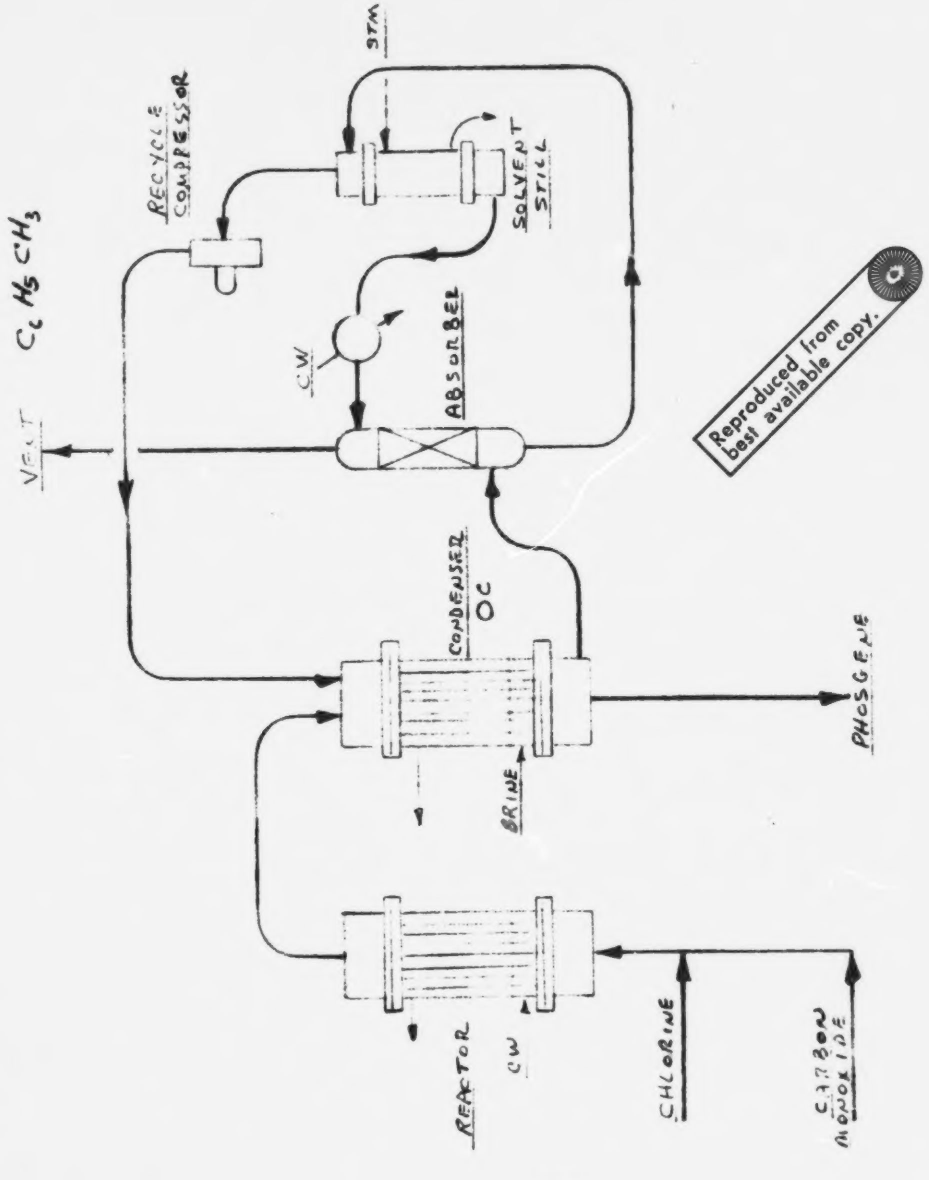
PR 109

FLOW SHEET

PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING
AND RESEARCH
CINCINNATI NEW YORK

Job EPA
Location CHLORINE
Subject PHOSGENE

File No. 03383 Sheet No. 1
Checked by ________ Date ________
Computed by SPK Date 11-4-71


STM
RECYCLE COMPRESSOR
SOLVENT STILL
$C_6H_5CH_3$
CW
ABSORBER
VENT
CONDENSER
0C
PHOSGENE
BRINE
REACTOR
CW
CHLORINE
CARBON MONOXIDE

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PROCESS: CHLORINATION OF CARBON MONOXIDE

PROCESS DATA TABULATION

SH 1 OF 2

SIC. NO.	INDUSTRY	PRODUCT
2819	Ioc	PHOSGENE COCl2

DATE:	PROCESS
10-29-71	CHLORINATION OF CARBON MONOXIDE

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒	2	8	1	8	
PRODUCT : COLS. 5-8	☒		1	2	6	
PROCESS : COLS. 9-13				4	2	

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
33	ALLIED	MOUNDSVILLE, WV	A	65	A
53	BSAF-WYANDOTTE	GEISMAR, LA	A	55	A
30	CHEMETRON	LAPORTE, TX	A	20	A
15	DUPONT	DEEPWATER, NJ	A	115	A
61	GENERAL ELECTRIC	MOUNT VERNON, IN	A	20	A
53	KAISER	GRAMERCY, LA	A	20	A
70	MOBAY	NEW MARTINSVILLE, WV	A	250	A
74	OLIN	ASHTABULA, OH	A	50	A

COMPUTER CODE NOS.

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AQCR 19–22	STATE 23 24	CITY 25–36	COMPANY 37–49	50 51	CAPACITY 52–55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

PROCESS DATA TABULATION

SH 2 OF 2

SIC. NO.	INDUSTRY	PRODUCT
DATE:	PROCESS	

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒					
PRODUCT : COLS. 5-8	☒					
PROCESS : COLS. 9-13						

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
195	OTT	MUSKEGON, MI	A	10	A
53	RUBICON	GEISMAR, LA	A	45	A
41	STAUFFER	COLD CREEK, LA	B	20	A
233	UNIONCARBIDE	INSTITUTE, WV	A	110	A
38	UPJOHN	LAPORTE, TX	A	200	A
24	VANDEMARK	LOCKPORT, NY	A	8	A

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 49	50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO. 2818	**INDUSTRY** IOC	**PRODUCT** PHOSGENE $COCl_2$	**COMPUTER CODE NOS.**
DATE PREPARED 10-29-71	**PROCESS** CHLORINATION OF CARBON MONOXIDE	**SOURCE** ABSORBER	

SIC. NO. : COLS. 1-4	☒	2	8	1	8	
PRODUCT : COLS. 5-8	☒		1	2	6	
PROCESS : COLS. 9-13				4	2	
SOURCE : COLS. 14-17	☒				1	

POLLUTANT / CONTROL DEVICE

DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
CO	NIL	C	NONE				
$COCl_2$	NIL	C	"				
$C_6H_5CH_3$	2.5	C	"				

COMPUTER CODE NOS.

18 PNO 20	21 CNO 23	24 UNCON EMISS 30	Q 31	32 CEF 35	Q 36	37 SOF 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ______________________

RELATED INDUSTRIES

BIBLIOGRAPHY

Product: Perchloroethylene (Tetrachloroethylene)

In 1970, 80 percent of the tetrachloroethylene production was made by the thermal chlorination of propane:

$$(C_3H_8) + 8Cl_2 \longrightarrow CCl_4 + C_2Cl_4 + 8HCl$$

The remaining 20 percent was made from acetylene, which is being phased out of DuPont's Niagara Falls Plant (60 millions of pounds per year) in 1972 and Detrex's Ashtabula Plant (25 millions of pounds per year) in 1971:

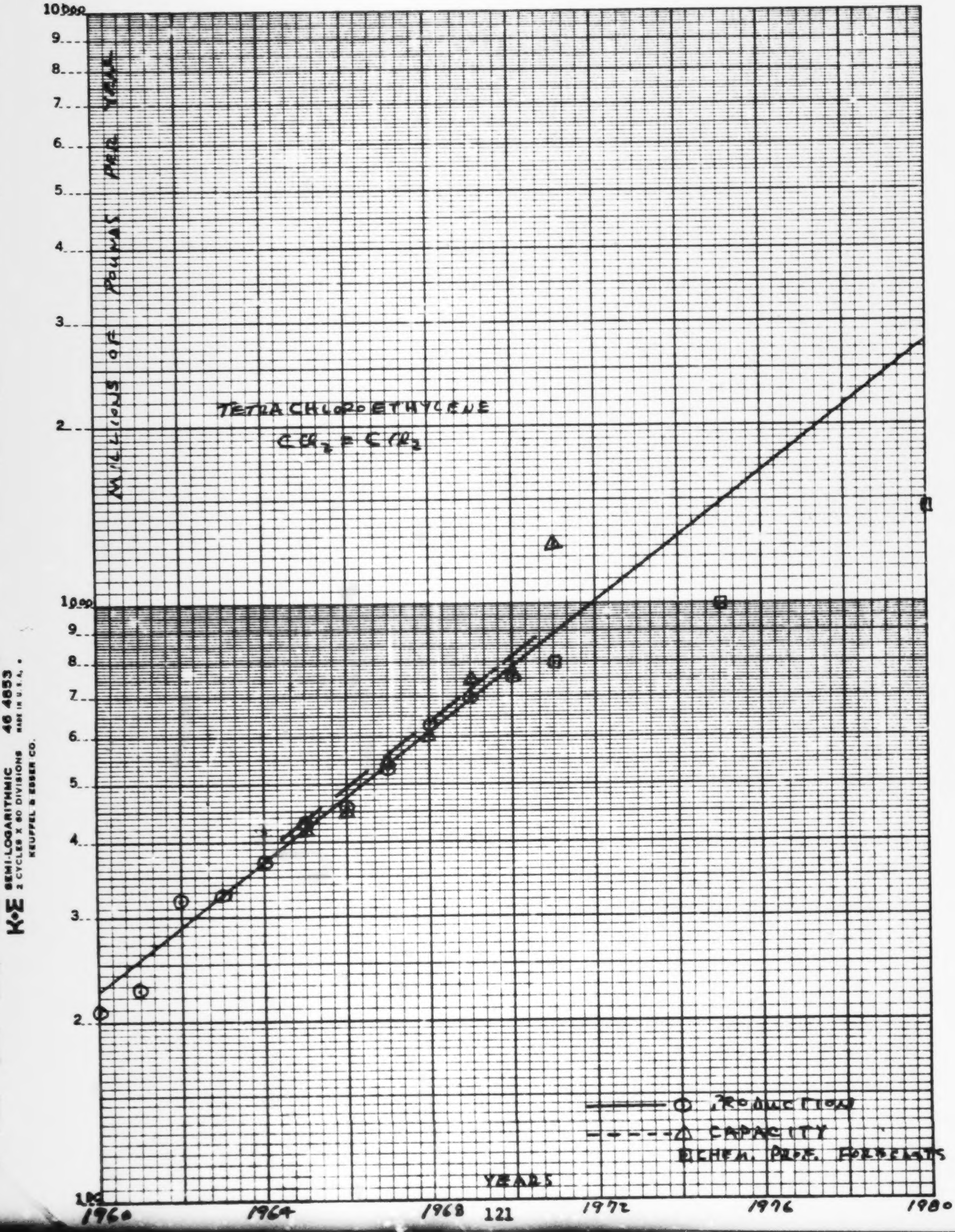
$$C_2HCl_3 + Cl_2 \longrightarrow C_2HCl_5$$

$$C_2HCl_5 \longrightarrow C_2Cl_4 + HCl$$

For the future, all tetrachloroethylene is expected to come from propane. Chart 15 shows the production and capacity data. In the sixties, the annual growth rate was over 12 percent. For the seventies, a 7 percent growth rate is expected.

73 percent of the tetrachloroethylene is used as a dry cleaning solvent. The second use is as a chemical intermediate.

CHART 15


MILLIONS OF POUNDS PER YEAR
10,000
9
8
7
6
5
4
3
2
1000
9
8
7
6
5
4
3
2
100
TETRACHLOROETHYLENE
$CCl_2 = CCl_2$
PRODUCTION
CAPACITY
□ CHEM. PROF. FORECASTS
YEARS
1960
1964
1968
1972
1976
1980
K+E SEMI-LOGARITHMIC 46 4853
2 CYCLES X 60 DIVISIONS MADE IN U.S.A.
KEUFFEL & ESSER CO.

Process: Thermal Chlorination of Propane

Fresh chlorine feed, together with recycled chlorine, and the propane feed are introduced into a vaporizer where they are mixed with recycled chlorides in the vapor space. The chlorine is in 10 to 25 percent excess, based on the propane. The recycle chloride diluent rate (controlled by heat input to the vaporizer) is designed to control adiabatic reactor temperature at 550 to 700C and is usually about 75 mole percent of the total stream; its composition also serves to control CCl_4-C_2Cl_4 ratio. The mixed gases, at atmospheric pressure, are fed to a refractory-lined reactor where they are rapidly mixed with the contents, thereby heated to ignition, and reacted adiabatically. The reaction is self-sustaining and supported by the considerable heat of reaction (after start-up), but is tempered and controlled by the diluent action of the recycle chlorides.

The reactor effluent is essentially free of unreacted hydrocarbon and consists mainly of carbon tetrachloride, perchloroethylene, HCl and excess chlorine. It is rapidly quenched by intimate contact with a liquid which is largely perchloroethylene. The rapid quench serves to preserve the equilibrium ratio attained in the reactor and prevents formation of undesirable by-products. It also serves to dissolve any quantities of hexachlorobenzene which may be present (these are small if reaction temperature is maintained below 650C) and which might introduce difficulties due to deposition of solids on heat transfer surfaces and in vessels. Some heat economy is obtained from the hot reactor effluent, which serves to boil the contents of the quench tank and thus provide boil-up for the CCl_4 column. Hexachlorobenzene is purged from the quench tank by allowing liquid to overflow to the recycle surge tank.

The CCl_4 column, operating on boil-up from the quench tank, returns quench liquid rich in perchloroethylene as a bottoms stream. Fractionation results in an overhead which is largely free of perchloroethylene. The condenser yields carbon tetrachloride, the desired quantity of which is withdrawn as product, the remainder being used as reflux. Chlorides-free gases (HCl and chlorine) are also disengaged at the overhead. These gases are scrubbed with water to remove HCl, the effluent liquor forming the aqueous HCl by-product. They are subsequently dried with concentrated sulfuric acid and purged to maintain the balance of inert gases; the remaining chlorine (with some uncondensed chlorides) is recycled to feed.

A perchloroethylene-rich stream is removed as a side stream from the CCl_4 column and processed to produce perchloroethylene product. Heavy ends are first removed by distillation and returned to the recycle surge tank. The overhead from the heavy ends column is fractionated in the C_2Cl_4 column where the desired quantity of perchloroethylene product is removed as the bottoms and the overhead (largely carbon tetrachloride) is sent to recycle.

The recycle surge tank serves as a reservoir for three recycle streams: (1) the quench tank overflow (largely perchloroethylene with some hexachlorobenzene), (2) heavy ends from the heavy ends column, and (3) the C_2Cl_4 column overhead (largely carbon tetrachloride). Proper control results in a recycle mixture of the desired composition, and this is fed to the vaporizer where the vapors are mixed with the feed materials.

To prevent buildup of hexachlorobenzene in the system, liquid is withdrawn from the vaporizer and sent to the heavies still. Here the more volatile components are stripped off and returned to the vaporizer, while heavy liquid consisting of hexachlorobenzene and some hexachloroethane is purged from the still pot.

The raw materials are propane, chlorine, catalyst ($CuCl_2$ and $BaCl_2$), water and sulfuric acid. The by-products are tetrachloroethylene (perchloroethylene), hexachlorobenzene, hydrogen chloride, hexachloroethane, and spent sulfuric acid.

There is one source of air pollution, the purge on the dry chlorine recycle, which removes inerts.

FR 100

FLOWSHEET

Job EPA

Location CHLORINE STUDY

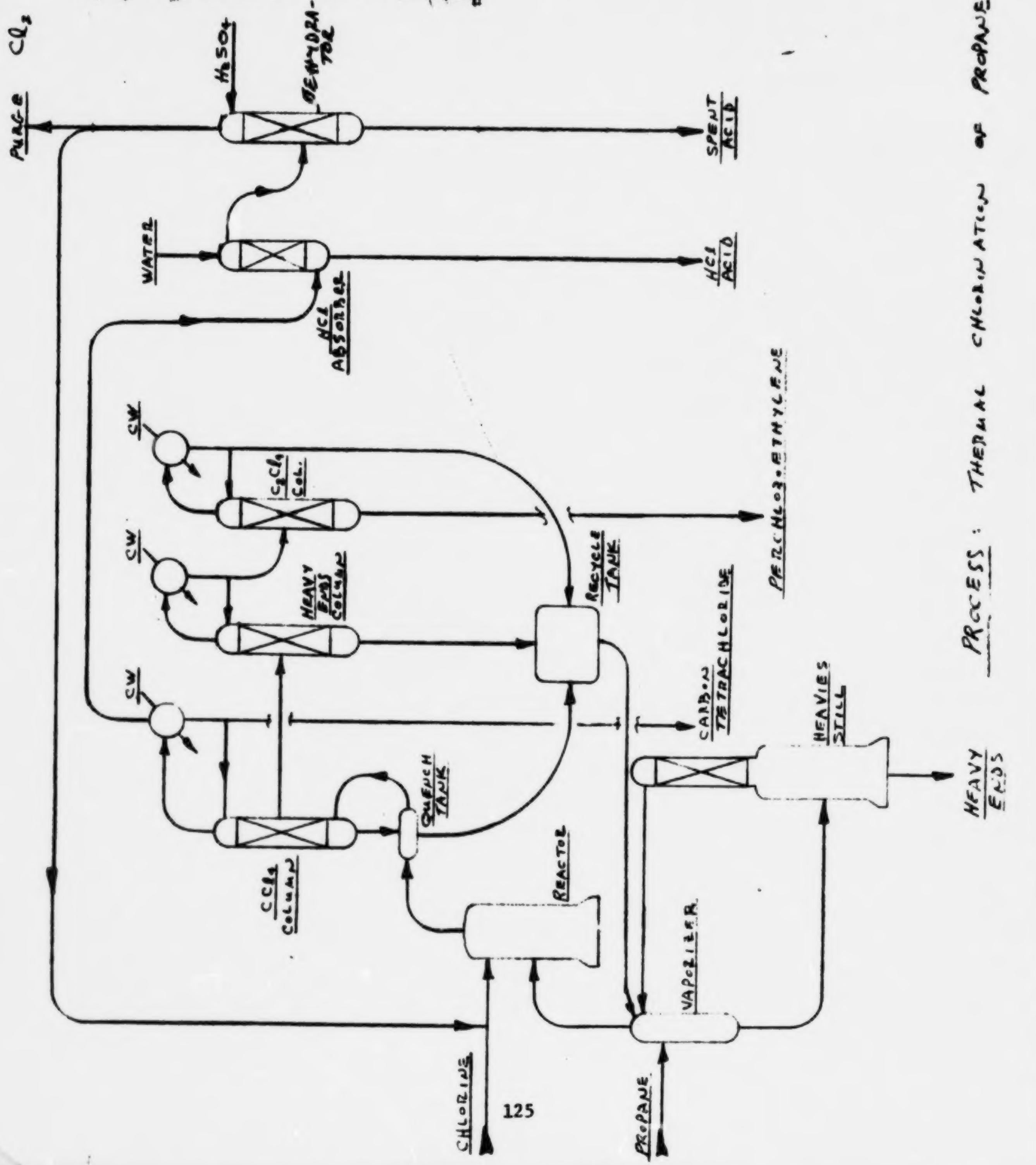
Subject CARBON TETRACHLORIDE AND PERCHLORETHYLENE

PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING AND RESEARCH
CINCINNATI NEW YORK

File No. 3383 Sheet No. 1

Checked by ______ Date ______

Computed by SPK Date 11-3-71



Cl_2
PURGE
H_2SO_4
DEHYDRATOR
SPENT ACID
WATER
HCl ABSORBER
HCl ACID
CW
C_2Cl_4 COL.
CW
HEAVY ENDS COLUMN
RECYCLE TANK
PERCHLOROETHYLENE
CW
CARBON TETRACHLORIDE
HEAVIES STILL
HEAVY ENDS
QUENCH TANK
CCl_4 COLUMN
REACTOR
VAPORIZER
CHLORINE
PROPANE

PROCESS: THERMAL CHLORINATION of PROPANE

PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO. 2818	INDUSTRY IOC	PRODUCT TETRACHLORO-ETHYLENE, C_2Cl_4
DATE: 10-27 '71	PROCESS THERMAL CHLORINATION OF PROPANE	

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒	2	8	1	8	
PRODUCT : COLS. 6-8	☒		1	3	[illegible]	
PROCESS : COLS. 9-13				3	[illegible]	

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
30	DIAMOND	DEER PARK, TX	A	100	A
39	DOW	FREEPORT, TX	A	120	A
31	DOW	PITTSBURG, CA	A	20	A
53	DOW	PLAQUEMINE, LA	A	150	A
53	ETHYL	BATON ROUGE, LA	A	50	A
53	HOOKER	TAFT, LA	B	35	A
53	PPG	LAKE CHARLES, LA	A	300	B
35	STAUFFER	LOUISVILLE, KY	A	70	A
53	VULCAN	GEISMAR, LA	A	110	A
253	VULCAN	WICHITA, KS	A	40	A
17	STAUFFER	DOMINGUEZ, CA	A	10	C

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 49	50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO. 2818	**INDUSTRY** IOC	**PRODUCT** TETRA-CHLOROETHYLENE C_2Cl_4	**COMPUTER CODE NOS.**
DATE PREPARED 10-29-71	**PROCESS** THERMAL CHLORINATION OF PROPANE	**SOURCE** DEHYDRATOR	

COMPUTER CODE NOS.

SIC. NO. :	COLS. 1-4	☒	2	8	1	8
PRODUCT :	COLS. 5-8	☒		1	3	0
PROCESS :	COLS. 9-13				3	5
SOURCE :	COLS. 14-17	☒			4	3

POLLUTANT			CONTROL DEVICE				
DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
Cl_2	20	C	NONE				

COMPUTER CODE NOS.

PNO 18-20	CNO 21-23	UNCON EMISS 24-30	Q 31	CEF 32-35	Q 36	SCF 37-40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ______

RELATED INDUSTRIES

BIBLIOGRAPHY

Process: Chlorination, Then Dehydrochlorination of Trichloroethylene

In a two-step process, trichloroethylene, made from acetylene, is reacted with chlorine in the liquid phase using pentachloroethane as the solvent and $SbCl_3$ as the catalyst. The conditions are 80C and about 2 pounds per square inch gage:

$$C_2HCl_3 + Cl_2 \longrightarrow C_2HCl_5$$

The pentachloroethane is then hydrolyzed at 80C in a column-type reactor using calcium hydroxide.

$$2C_2HCl_5 + Ca(OH)_2 \longrightarrow 2C_2Cl_4 + CaCl_2 + 2H_2O$$

The products from the hydrolyzer are fed to a stripper where the lights are removed. The bottoms from the stripper are fed to a fractionator where the product, C_2Cl_4, is taken off overhead and where the bottoms are heavies. Yields are about 90 percent.

The raw materials are chlorine, trichloroethylene and calcium hydroxide. The by-products are heavies and calcium chloride.

The only source of air pollutants is the inerts purge on the reflux condenser atop the reactor.

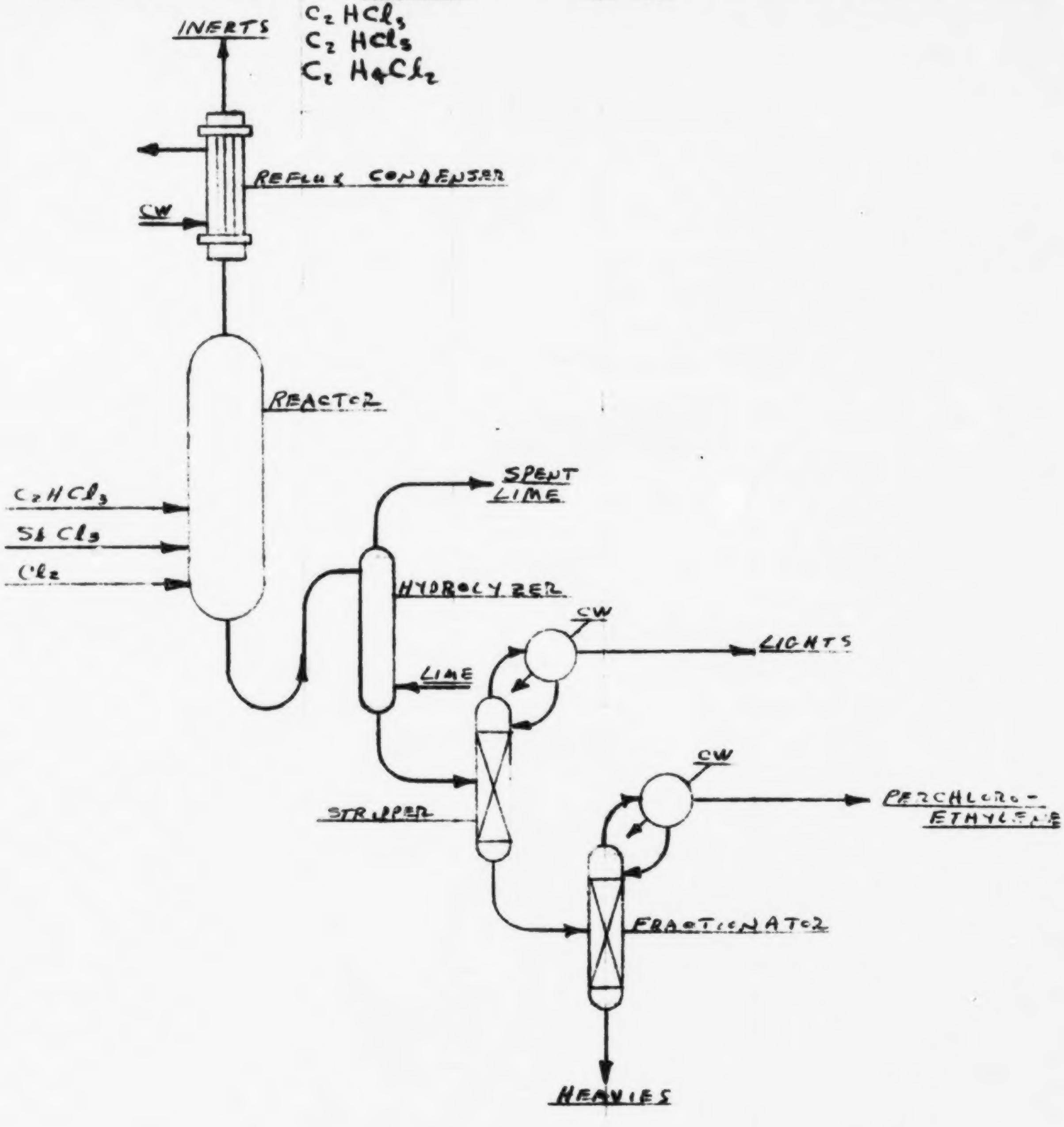
PR 109

FLOWSHEET

PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING AND RESEARCH
CINCINNATI NEW YORK

Job EPA
Location CHLORINE STUDY
Subject PERCHLORO ETHANE

File No. 3383 Sheet No. 1
Checked by ____ Date ____
Computed by SDK Date 11-23-71


INERTS
C_2HCl_3
C_2HCl_5
$C_2H_4Cl_2$
REFLUX CONDENSER
CW
REACTOR
C_2HCl_3
$SbCl_3$
Cl_2
SPENT LIME
HYDROLYZER
LIME
CW
LIGHTS
STRIPPER
CW
PERCHLORO-ETHYLENE
FRACTIONATOR
HEAVIES

PROCESS: CHLORINATION THEN DEHYDROCHORINATION
TRICHLOROETHYLENE

PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO.	INDUSTRY	PRODUCT
2818	IOC	TETRACHLORO ETHANE, C_2Cl_4

DATE:	PROCESS
11-22-71	CHLORINATION—DEHYDROCHLORINATION OF C_2HCl_3

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒	2	8	1	8	
PRODUCT : COLS. 5-8	☒		1	3	0	
PROCESS : COLS. 9-13				6	6	

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
74	DETREX	ASHTABULA, OH	A	25	A
24	DuPONT	NIAGARA FALLS, NY	A	60	A
32	HOOKER	TACOMA, WA	A	5	A
22	PPG	BARBERTON, OH	A	20	A

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 49	50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO. 2818	**INDUSTRY** IOC	**PRODUCT** TETRACHLORO ETHYLENE, C_2Cl_4	
DATE PREPARED 11-22-71	**PROCESS** CHLORINATION -DEHYDROCHLORINATION OF TRICHLOROETHYLENE	**SOURCE** REFLUX CONDENSER	

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒	2	8	1	8
PRODUCT : COLS. 5-8	☒		1	3	0
PROCESS : COLS. 9-13				6	6
SOURCE : COLS. 14-17	☒			4	2

POLLUTANT / CONTROL DEVICE

DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
C_2HCl_3	5.6	C	NONE				
C_2HCl_5	0.6	C	"				
$C_2H_4Cl_2$	4.7	C	"				

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23	UNCON EMISS 24 30	Q 31	CEF 32 35	Q 36	SCF 37 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ______________________

RELATED INDUSTRIES

BIBLIOGRAPHY

Product: Trichloroethylene

Trichloroethylene is an old compound produced by a well-established process based on acetylene. Over 90 percent of the trichloroethylene is made by this dual step process:

Chlorination of acetylene:

$$2Cl_2 + C_2H_2 \longrightarrow C_2H_2Cl_4$$

followed by dehydrochlorination:

$$C_2H_2Cl_4 \longrightarrow C_2HCl_3 + HCl$$

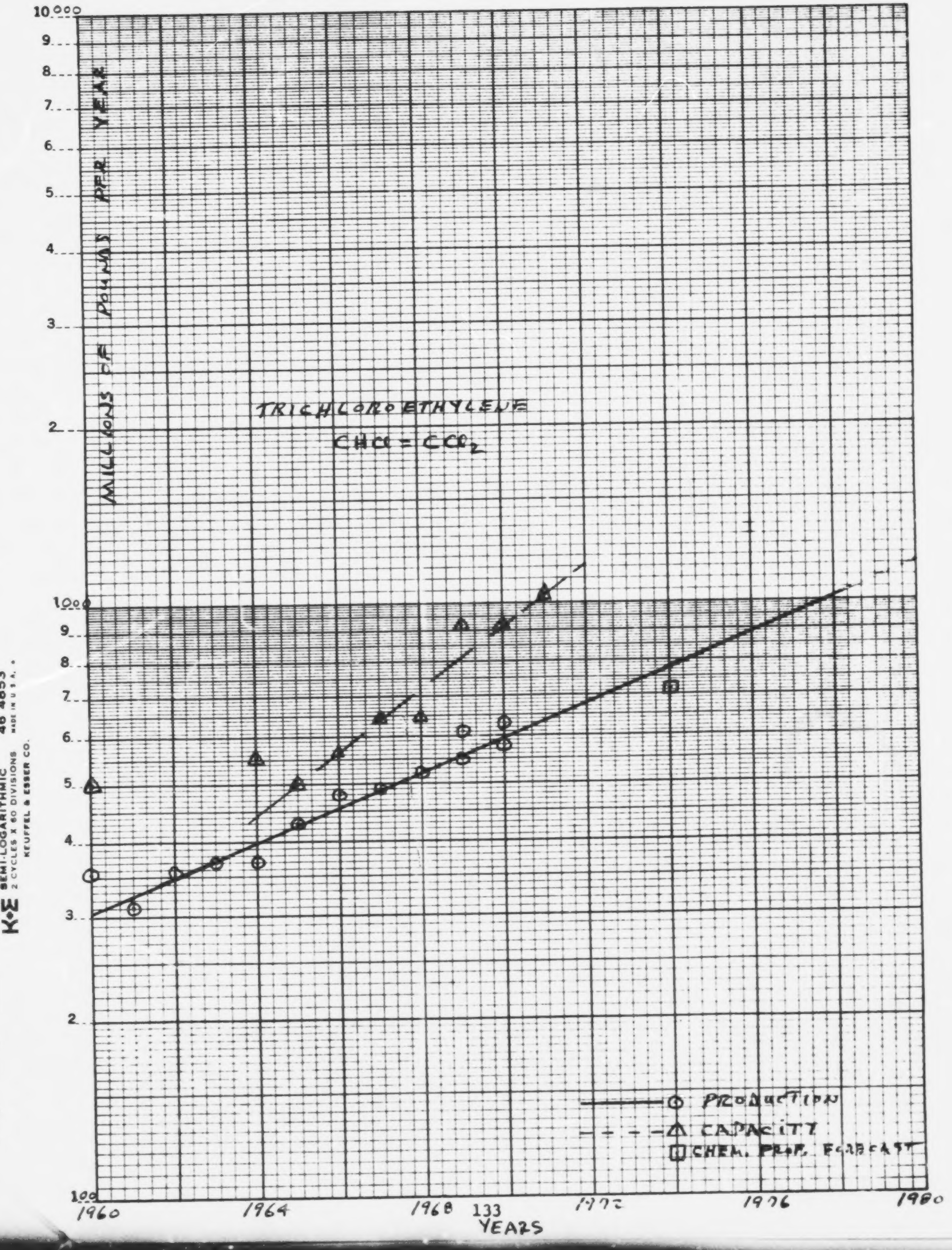
The remaining 10 percent of the trichloroethylene is made by the oxychlorination of 1,2-dichloroethane:

$$O_2 \text{ (air)} + HCl + C_2H_4Cl_2 \longrightarrow C_2HCl_3 + 2H_2O$$

This process will probably increase in capacity, phasing out the acetylene-based plants.

Chart 16 shows the production and capacity data. In the past, the annual growth rate was about 5 percent, but this rate is expected to decline to about 3-1/2 percent per year in the seventies. Over 90 percent of the trichloroethylene is used in metal degreasing. The rest is used in solvent extractions such as making decaffeinated coffee.

CHART 16


10.000
9
8
7
6
5
4
3
2
1.000
9
8
7
6
5
4
3
2
100
MILLIONS OF POUNDS PER YEAR
TRICHLOROETHYLENE
CHCl = CCl$_2$
PRODUCTION
CAPACITY
CHEM. PROF. FORECAST
1960
1964
1968
1972
1976
1980
YEARS
K+E SEMI-LOGARITHMIC 46 4853
2 CYCLES X 60 DIVISIONS MADE IN U.S.A.
KEUFFEL & ESSER CO.

Process: Chlorination, then Dehydrochlorination of Acetylene

High purity chlorine gas, containing no oxygen, is fed with acetylene into a packed tower in which tetrachloroethane is refluxing. The pressure is atmospheric and the temperature is about 50C. The tower is equipped with a reflux condenser. The chlorine and acetylene react to form tetrachloroethane. The tetrachloroethane is withdrawn from the reactor, vaporized, superheated to 300C, and fed to the dehydrochlorinator (which is a tower filled with activated carbon), yielding trichloroethylene. The temperature is 300C, and the pressure is atmospheric. The hydrogen chloride, trichloroethylene, and unconverted tetrachloroethane from the dehydrochlorinator, are fed to a stripping column where the HCl is stripped off overhead and absorbed in water as hydrochloric acid. The conversion of the tetrachloroethane is about 90 percent. The bottoms are fed to a second stripper where the product, trichloroethylene, is taken off overhead. These bottoms are fed to a third stripper, where the by-product perchloroethylene is taken off overhead. These last bottoms are fed to a fractionator where the tetrachloroethane is taken off overhead and recycled. The bottoms from the fractionator are discarded.

The raw materials are chlorine (high purity, oxygen-free), acetylene, and water. The by-products are perchloroethylene, hydrogen chloride, and heavies.

In the process for producing trichloroethylene, there are two sources of air pollution, the vent on the reflux condenser connected to the reactor, and the vent on the tail gas absorber.

PR 10P

FLOWSHEET

Job EPA

Location CHLORINE STUDY

Subject TRICHLOROETHYLENE

PROCESSES RESEARCH, INC.

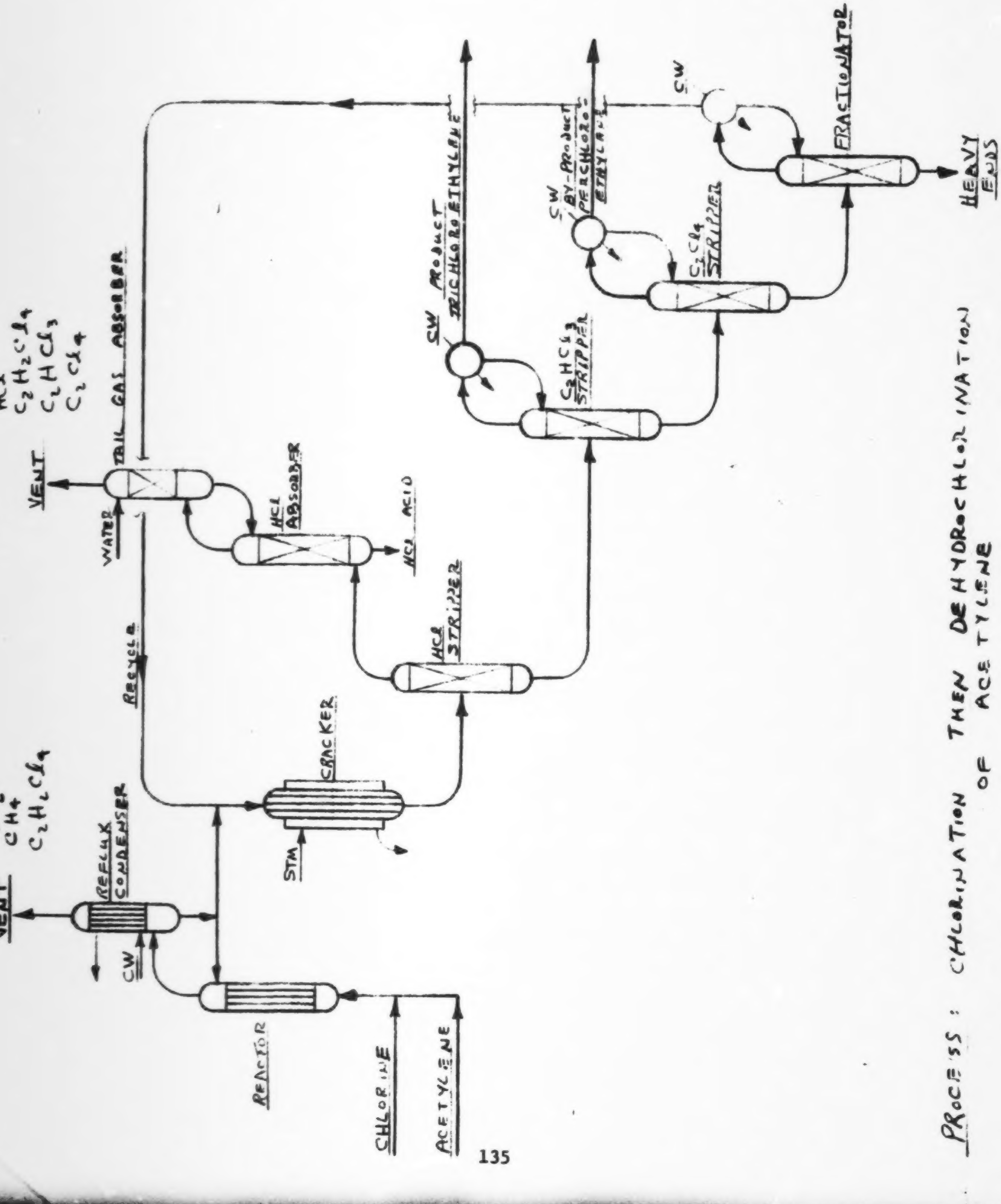
INDUSTRIAL PLANNING
AND RESEARCH

CINCINNATI NEW YORK

File No. 3383 Sheet No. 1

Checked by ____ Date ____

Computed by SPK Date 11-9-7


CHLORINE
ACETYLENE
REACTOR
CW
REFLUX CONDENSER
VENT
C_2H_6
CH_4
$C_2H_2Cl_4$
STM
CRACKER
RECYCLE
HCl STRIPPER
WATER
HCl ABSORBER
HCl ACID
TAIL GAS ABSORBER
VENT
HCl
$C_2H_2Cl_4$
C_2HCl_3
C_2Cl_4
C_2HCl_3 STRIPPER
SW
PRODUCT TRICHLOROETHYLENE
C_2Cl_4 STRIPPER
SW
BY-PRODUCT PERCHLOROETHYLENE
SW
FRACTIONATOR
HEAVY ENDS

PROCESS: CHLORINATION THEN DEHYDROCHLORINATION OF ACETYLENE

PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO.	INDUSTRY	PRODUCT
2818	IOC	TRICHLOROETHYLENE C_2HCl_3

DATE:	PROCESS
11-1-71	CHLORINATION OF ACETYLENE FOLLOWED BY DEHYDROCHLORINATION

COMPUTER CODE NOS.

SIC. NO. :	COLS. 1-4	☒	2	8	1	8
PRODUCT :	COLS. 5-8	☒		1	2	9
PROCESS :	COLS. 9-13				4	5

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
74	DETREX	ASHTABULA, OH	A	100	A
39	DIAMOND	DEER PARK, TX	A	60	A
24	DuPONT	NIAGARA FALLS, NY	A	275	A
24	HOOKER	NIAGARA FALLS, NY	A	60	A
32	HOOKER	TACOMA, WA	A	30	A
53	HOOKER	TAFT, LA	B	40	A
53	ETHYL	BATON ROUGE, LA	A	40	A
22	PPG	BARBERTON, OH	A	45	B

COMPUTER CODE NOS.

AQCR 19-22	STATE 23-24	CITY 25-36	COMPANY 37-49	☒ 50-51	CAPACITY 52-55	Q 56	YEAR 57-58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO. 2818	**INDUSTRY** IOC	**PRODUCT** TRICHLOROETHYLENE C_2HCl_3	**COMPUTER CODE NOS.**
DATE PREPARED 11-1-71	**PROCESS** CHLORINATION THEN DEHYDROCHLORINATION OF ACETYLENE	**SOURCE** REFLUX CONDENSER	

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒	2	8	1	8
PRODUCT : COLS. 5-8	☒		1	2	9
PROCESS : COLS. 9-13				4	5
SOURCE : COLS. 14-17	☒			4	2

POLLUTANT / CONTROL DEVICE

DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
C_2H_6	2.5	C	NONE				
CH_4	2.5	C	"				
$C_2H_2Cl_4$	1.0	C	"				

COMPUTER CODE NOS.

PNO 18–20	CNO 21–23	UNCON EMISS 24–30	Q 31	CEF 32–35	Q 36	SCF 37–40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ______

RELATED INDUSTRIES

BIBLIOGRAPHY

SOURCE DATA TABULATION

INDUSTRY NO. 2818	**INDUSTRY** IOC	**PRODUCT** TRICHLOROETHYLENE C_2HCl_3	
DATE PREPARED 11-1-71	**PROCESS** CHLORINATION THEN DEHYDROCHLORINATION OF ACETYLENE	**SOURCE** TAIL GAS ABSORBER	

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒	2	8	1	8
PRODUCT : COLS. 5-8	☒		1	2	9
PROCESS : COLS. 9-13				4	5
SOURCE : COLS. 14-17	☒			4	1

POLLUTANT

CONTROL DEVICE

DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
HCl	0.2	C	NONE				
$C_2H_2Cl_4$	0.1	C	"				
C_2HCl_3	0.7	C	"				
C_2Cl_4	0.2	C	"				

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23	UNCON EMISS 24 30	Q 31	CEF 32 35	Q 36	SCF 37 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING

RELATED INDUSTRIES

BIBLIOGRAPHY

Process: Oxyhydrochlorination of Dichloroethane

Dichloroethane is oxychlorinated by air and hydrogen chloride to produce trichloroethylene. With the hydrogen chloride in excess, air, hydrogen chloride, and dichloroethane are mixed and reacted in the vapor phase in a tubular reactor at 300 to 400C and about 100 pounds per square inch gage. The reaction is exothermic, requiring cooling of the reactor. The reaction products are scrubbed with caustic, condensing the product and absorbing the excess HCl. The unreacted air is vented.

The crude product is decanted from the scrubber fluid and fed to a stripper. In the stripper, the product is stripped from the heavies and is fed to a fractionator. In the fractionator, pure product, trichloroethylene, is taken as bottoms.

The raw materials are dichloroethane, hydrogen chloride, caustic, and air. The by-products are spent caustic, heavies, and a small amount of lights. The yields are estimated at 90 percent.

There is a single source of air pollutants, the spent air vent on the absorber.

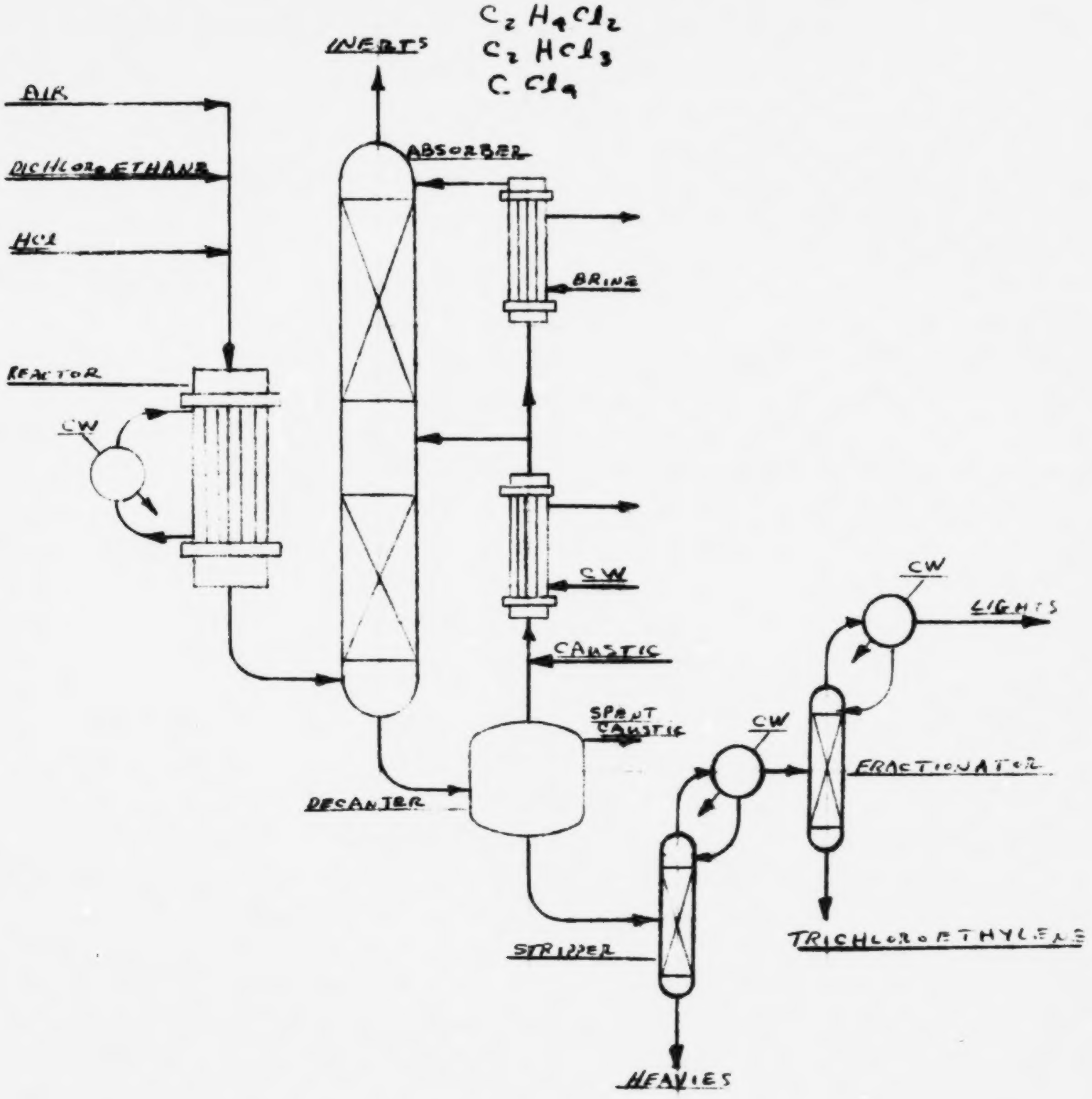
PR 109

FLOWSHEET

PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING AND RESEARCH
CINCINNATI NEW YORK

Job EPA
Location CHLORINE STUDY
Subject TRICHLORO ETHYLENE

File No. 3383 Sheet No 1
Checked by ______ Date ______
Computed by SPK Date 11-23-71


$C_2H_4Cl_2$
C_2HCl_3
CCl_4
INERTS
AIR
DICHLORO ETHANE
HCl
ABSORBER
BRINE
REACTOR
CW
CW
CAUSTIC
SPENT CAUSTIC
CW
LIGHTS
CW
FRACTIONATOR
DECANTER
STRIPPER
TRICHLOROETHYLENE
HEAVIES

PROCESS: OXYHYDROCHLORINATION OF DICHLOROETHANE

PROCESS DATA TABULATION

SH____OF_____

SIC. NO.	INDUSTRY	PRODUCT
2818	IOC	TRICHLORO-ETHYLENE

DATE:	PROCESS
11-22-71	OXYCHLORINATION OF DICHLORO ETHANE

COMPUTER CODE NOS.

SIC. NO. :	COLS. 1-4	☒	2	8	1	8
PRODUCT :	COLS. 5-8	☒		1	2	9
PROCESS :	COLS. 9-13				6	7

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
58	Dow	FREEPORT, TX	A	200	A
53	Dow	PLAQUEMINE, LA	A	35	A
53	PPG	LAKE CHARLES, LA	A	200	A

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 49	50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO. 2818	**INDUSTRY** IOC	**PRODUCT** TRICHLORO ETHYLENE	
DATE PREPARED 11-23-71	**PROCESS** OXYCHLOR-INATION OF DICHLOROETHANE	**SOURCE** ABSORBER	

COMPUTER CODE NOS.

SIC. NO. :	COLS. 1-4	☒	2	8	1	8
PRODUCT :	COLS. 5-8	☒		1	2	9
PROCESS :	COLS. 9-13				6	7
SOURCE :	COLS. 14-17	☒				1

POLLUTANT / CONTROL DEVICE

DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
$C_2H_4Cl_2$	26	C	NONE				
C_2HCl_3	57	C	"				
CCl_4	26	C	"				
C_2Cl_4	NIL	C	"				

COMPUTER CODE NOS.

PNO 18-20	CNO 21-23	UNCON EMISS 24-30	Q 31	CEF 32-35	Q 36	SCF 37-40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING

RELATED INDUSTRIES

BIBLIOGRAPHY

2. Industrial Inorganic Chemicals Not Elsewhere Classified - SIC Industry No. 2819

Establishments primarily engaged in manufacturing industrial inorganic chemicals not elsewhere classified. Important products of this industry include inorganic salts, inorganic compounds such as alums, peroxides, carbides, and ammonia, rare earth metal salts, and elements.

Some of the chlorine products of this industry include:

Aluminum chloride
Ammonium chloride
Ammonium perchlorate
Bleaching powder
Brine
Calcium chloride
Calcium hypochlorite
Calomel
Chlorosulfonic acid
Cobalt chloride
Ferric chloride
Hydrochloric acid
Indium chloride
Lime bleaching compounds
Magnesium chloride
Mercury chlorides
Potassium chloride
Perchloric acid
Potassium chlorate
Potassium hypochlorate
Radium chloride
Sodium chlorate
Sodium hypochlorite
Sulfur chloride
Tin chloride
Zinc chloride

This industry is not a big consumer of chlorine or its compounds. Only hydrogen chloride has been included in this study.

Product: Hydrogen Chloride

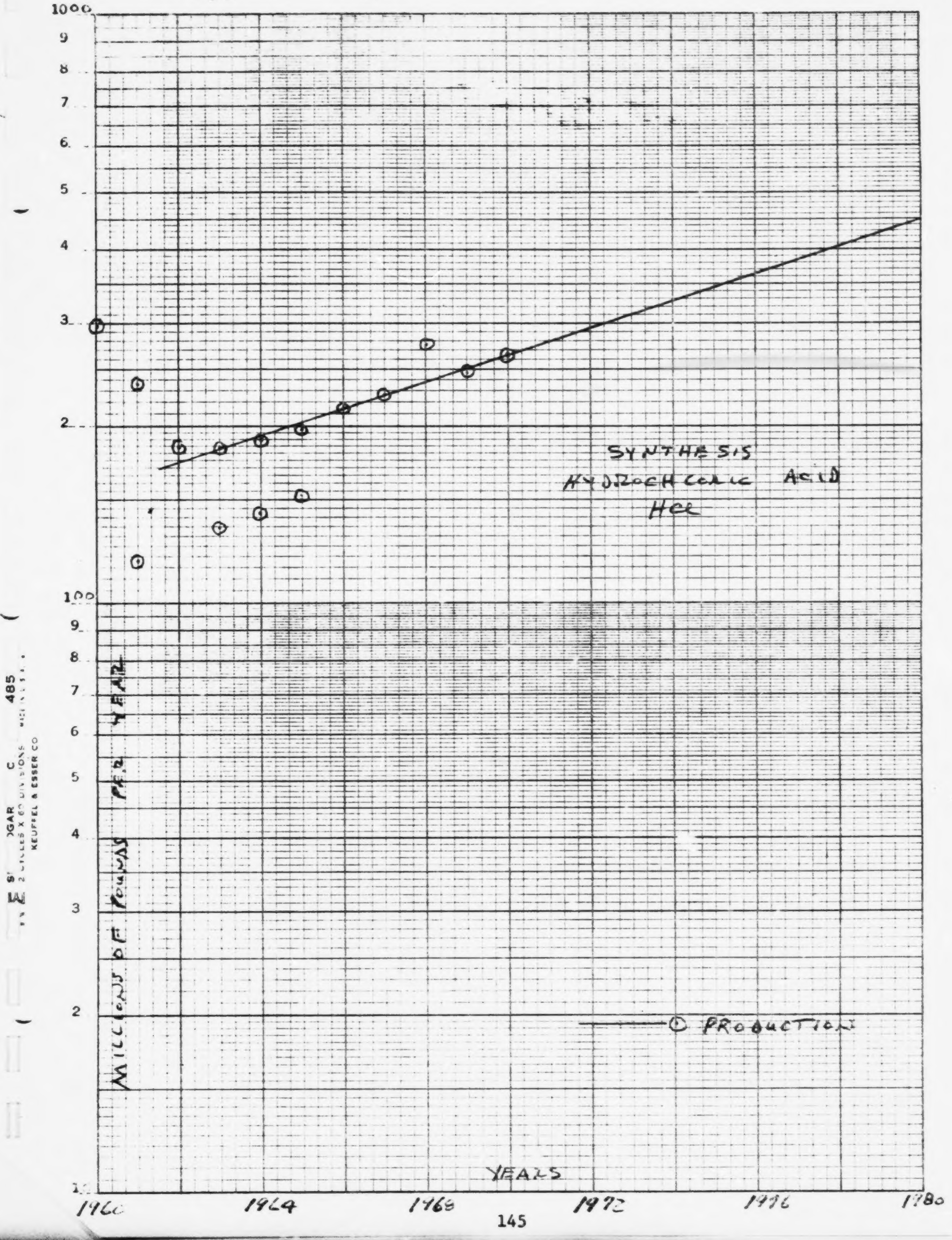
In 1970, about 7 percent of the nearly 4 billion pounds of total hydrogen chloride production came from chlorinating hydrogen, or 265 million pounds of 100 percent HCl:

$$H_2 + Cl_2 \longrightarrow 2HCl$$

About an equal amount of hydrogen chloride is produced as a by-product from salt cake production. The chlorination of organic chemicals produces the remaining 85 percent of the hydrogen chloride, as a by-product. Chart 11 shows the synthetic hydrogen chloride production. Little or no growth is expected in synthetic hydrogen chloride production.

Hydrogen chloride has many uses. The metal industries use vast quantities. As an acid, it is replacing sulfuric acid as a pH adjusting reagent. Because of its nontoxicity, the food industry uses hydrogen chloride extensively.

CHART 11


1000
9
8
7
6
5
4
3
2
100
9
8
7
6
5
4
3
2
10
MILLIONS OF POUNDS PER YEAR
SYNTHESIS
HYDROCHLORIC ACID
HCl
PRODUCTION
YEARS
1960
1964
1968
1972
1976
1980
485
2 CYCLES X 60 DIVISIONS
KEUFFEL & ESSER CO

Process: Chlorination of Hydrogen

Dry chlorine and hydrogen gases, with the H_2 in 2 to 5 percent excess, are fed to a burner and burned in a hydrogen-chlorine flame. The hot gases are passed to a water-cooled chamber which operates at near atmospheric pressure and then cooled to 300F. The HCl gas is then passed to a cooler-absorber where 20°Be hydrochloric acid is produced. The inerts and excess hydrogen, which are vented through the tail gas absorber, are the only air pollutants.

The raw materials are hydrogen, chlorine, and water. There are no by-products.

[illegible]

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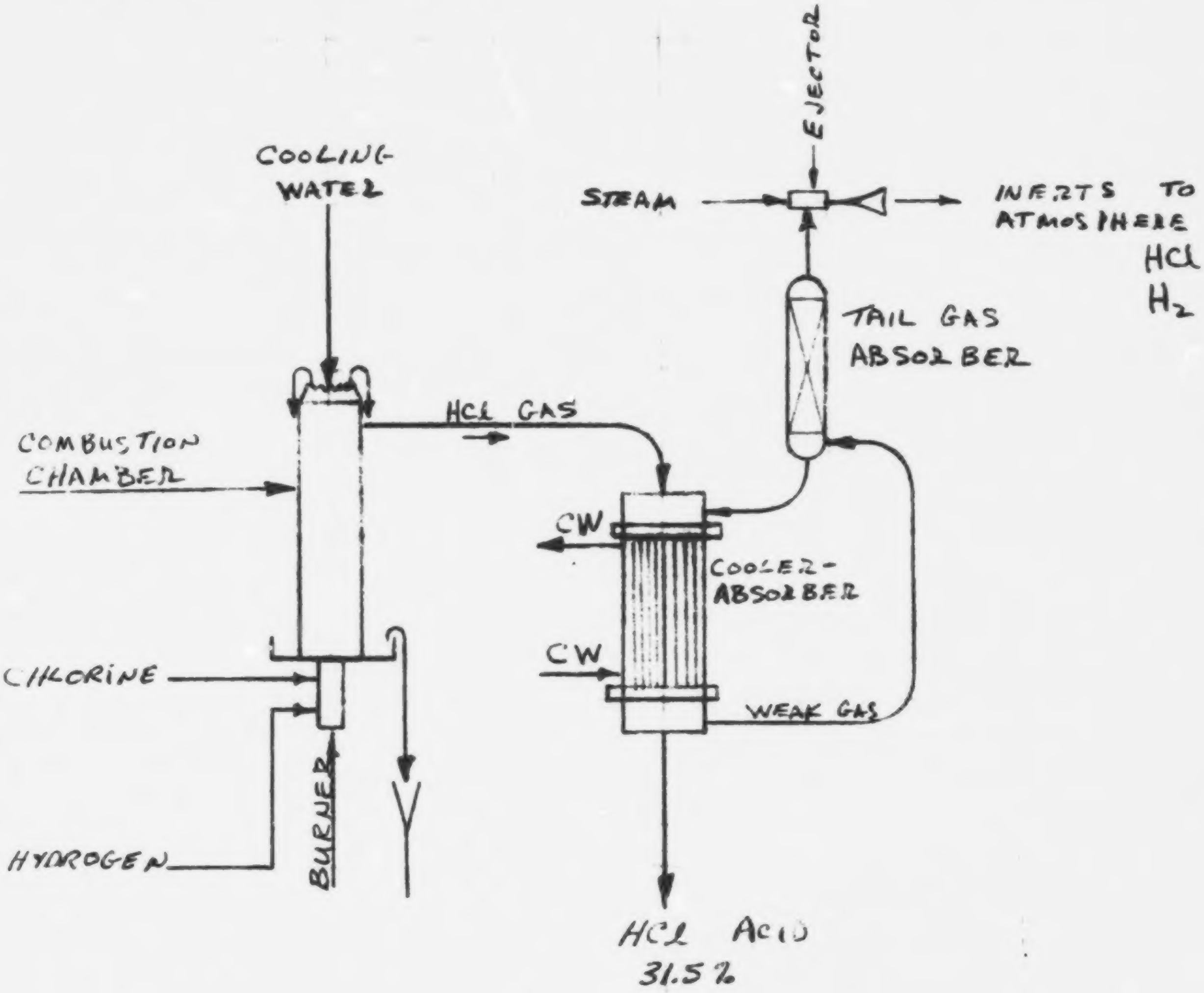
Job EPA
Location CHLORINE STUDY
Subject HYDROGEN CHLORIDE

File No 03383 Sheet No 1
Checked by ______ Date ______
Computed by SPK Date 11-3-71



EJECTOR
COOLING WATER
STEAM
INERTS TO ATMOSPHERE
HCl
H_2
TAIL GAS ABSORBER
HCL GAS
COMBUSTION CHAMBER
CW
COOLER-ABSORBER
CW
CHLORINE
WEAK GAS
BURNER
HYDROGEN
HCL ACID
31.5%

PROCESS DATA TABULATION

SH 1 OF 2

SIC. NO. 2819	INDUSTRY IIC	PRODUCT HYDROGEN CHLORIDE
DATE: 10-28-71	PROCESS CHLORINATION OF HYDROGEN	

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒	2	8	1	9
PRODUCT : COLS. 5-8	☒		1	2	2
PROCESS : COLS. 9-13				4	0

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
12[illegible]	ALLIED	SYRACUSE, NY	C		
71	ALLIED	BRUNSWICK, GA	C		
53	ALLIED	BATON ROUGE, LA	C		
24	HOOKER	NIAGARA FALLS, NY	C		
32	HOOKER	TACOMA, WA	C		
195	HOOKER	MONTAGUE, MI	C		
24	STAUFFER	NIAGARA FALLS, NY	C		
19	STAUFFER	DOMINGUEZ, CA	C		
69	PENN WALT	CALVERT CITY, KY	C		
3[illegible]	PENN WALT	WYANDOTTE, MI	C		
32	PENN WALT	TACOMA, WA	C		

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 49	50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

PROCESS DATA TABULATION

SH 2 OF 2

SIC. NO.

INDUSTRY

PRODUCT

DATE:

PROCESS

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4 ☒

PRODUCT : COLS. 5-8 ☒

PROCESS : COLS. 9-13

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
53	ETHYL	BATON ROUGE, LA	C		
38	ETHYL	HOUSTON, TX	C		
38	DIAMOND	HOUSTON, TX	C		
22	DIAMOND	PAINESVILLE, OH	C		
30	DOW	FREEPORT, TX	C		
21	DOW	PITTSBURG, CA	C		
145	HERCULES	HOPEWELL, VA	C		
253	VULCAN	WICHITA, KS	C		

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 49	50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO. 2819	**INDUSTRY** IIC	**PRODUCT** HYDROGEN CHLORIDE, HCl	**COMPUTER CODE NOS.**
DATE PREPARED 10-28-71	**PROCESS** CHLORINATION OF HYDROGEN	**SOURCE** TAIL GAS ABSORBER	

SIC. NO. :	COLS. 1-4	☒	2	8	1	9
PRODUCT :	COLS. 5-8	☒		1	2	2
PROCESS :	COLS. 9-13				4	0
SOURCE :	COLS. 14-17	☒			4	1

POLLUTANT | CONTROL DEVICE

DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
HCl	0.1	C	NONE				
H_2	1	C	NONE				

COMPUTER CODE NOS.

PNO 18-20	CNO 21-23	UNCON EMISS 24-30	Q 31	CEF 32-35	Q 36	SCF 37-40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ______________________

RELATEC INDUSTRIES

BIBLIOGRAPHY

3. Plastic Materials - SIC Industry No. 2819

Establishments primarily engaged in manufacturing synthetic resins. Important products of this industry include the following resins: phenolic urea, vinyl, styrene, acrylic polethylene, polypropylene, and silicones.

Some of the chlorinated compounds of this industry include:

Epoxy resins
Polyvinyl chloride resins

Of this industry (No. 2819), only polyvinyl chloride resins are big consumers of chlorine or chlorinated compounds.

Product: Vinyl Chloride

In 1970, less than 20 percent of the vinyl chloride production was made by this acetylene-based process:

$$HCl + C_2H_2 \longrightarrow C_2H_3Cl$$

This older reaction is being replaced by an ethylene dichloride based process, which will also be studied:

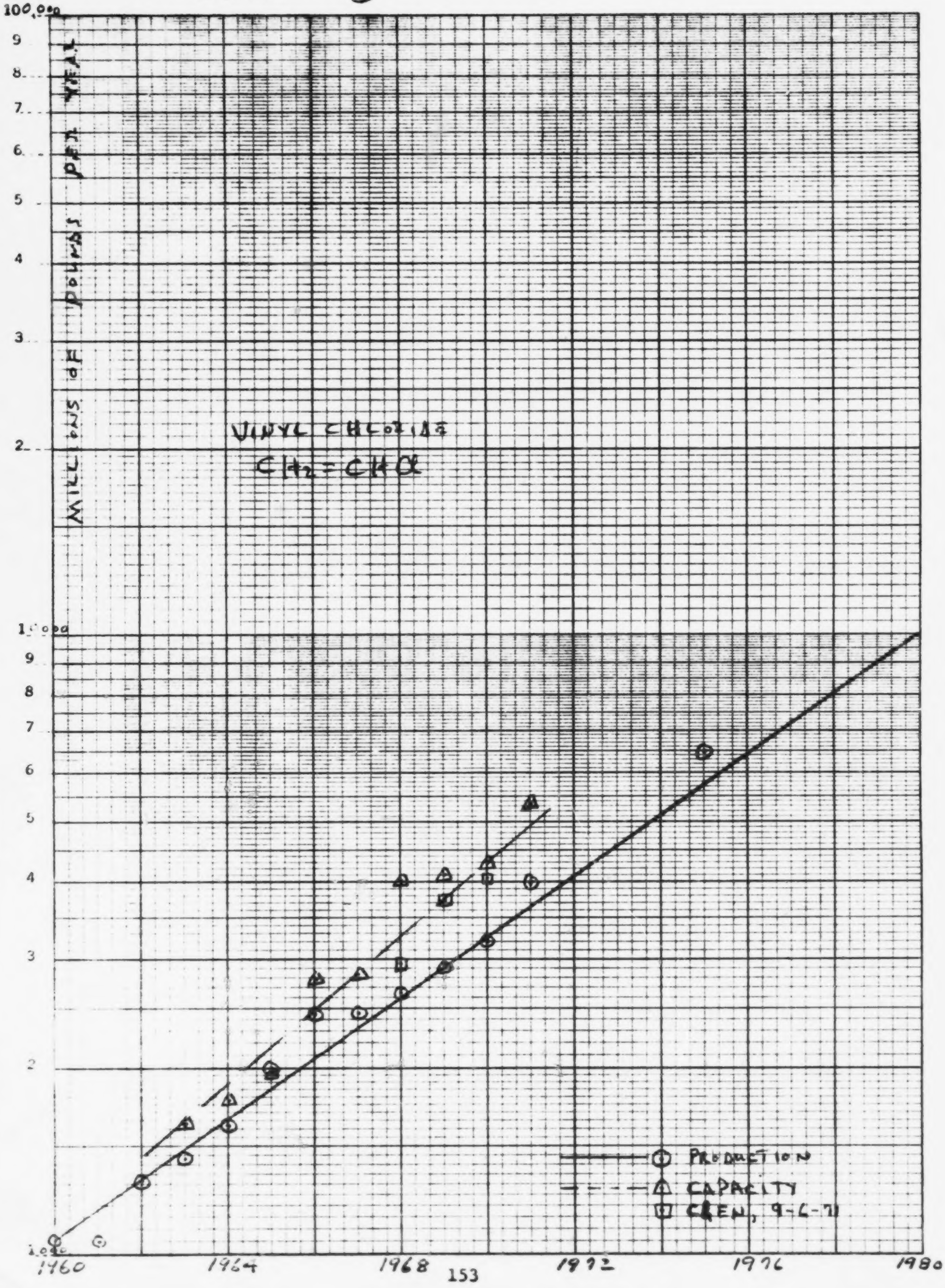
$$C_2H_4Cl_2 \longrightarrow C_2H_3Cl + HCl$$

This is a thermal cracking reaction carried out at 900C and low pressures.

Less than 4 percent of the vinyl chloride is made by a combination of the two processes.

Chart 8 shows the production and capacity for vinyl chloride. The future growth rate is estimated at 13 percent per year, or a production of 10 billion pounds per year by 1980. Vinyl chloride is used to make polyvinyl chloride and its copolymers.

CHART 8


MILLIONS OF POUNDS PER YEAR
VINYL CHLORIDE
$CH_2=CHCl$
100,000
9
8
7
6
5
4
3
2
10,000
9
8
7
6
5
4
3
2
1,000
1960
1964
1968
1972
1976
1980
PRODUCTION
CAPACITY
C&EN, 9-6-71

FR 107

Job EPA

Location CHLORINE STUDY

Subject VINYL CHLORIDE

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File No. 3383 Sheet No. 1

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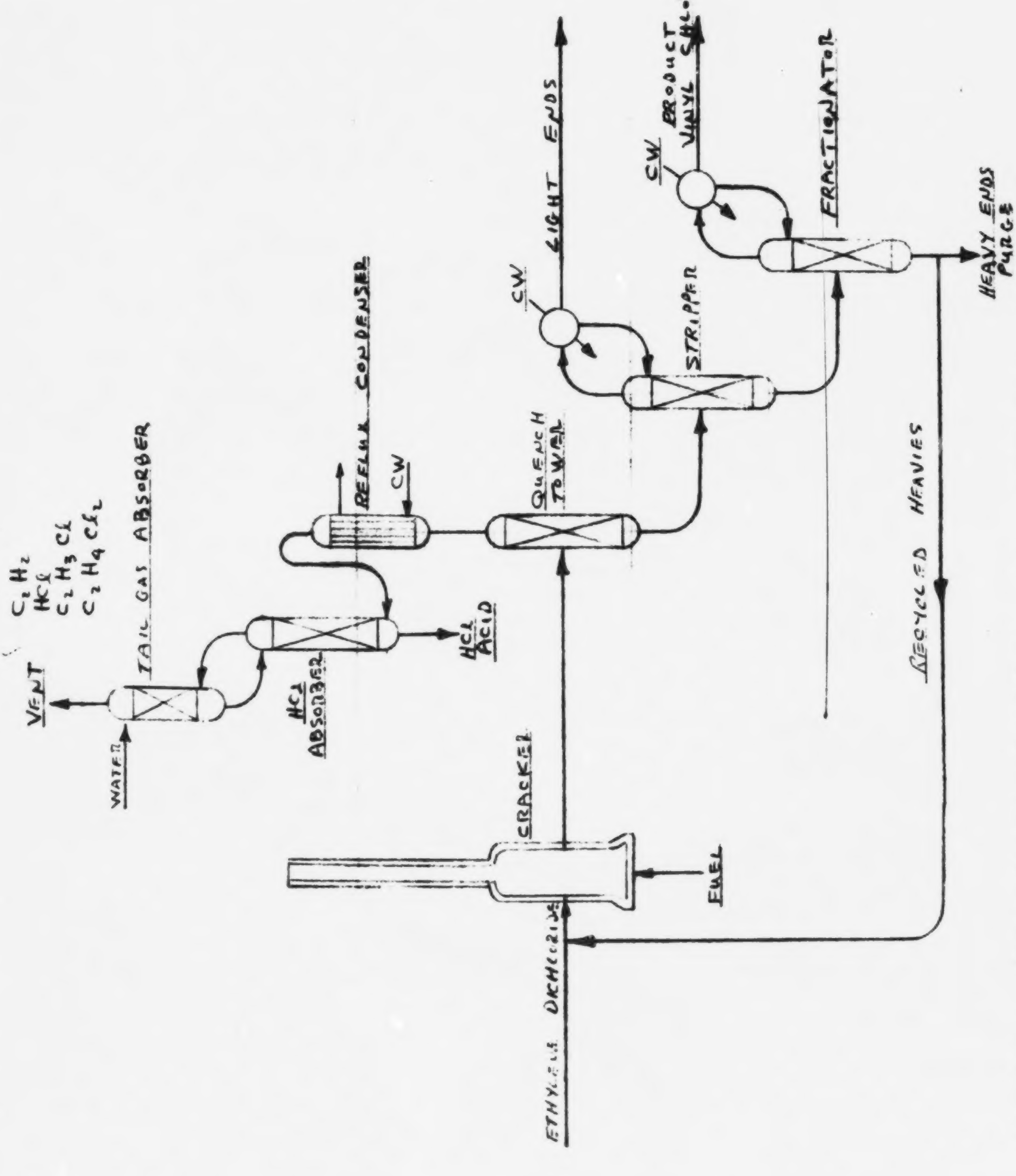
VENT
WATER
TAIL GAS ABSORBER
C_2H_2
HCl
C_2H_3Cl
$C_2H_4Cl_2$
HCl ABSORBER
HCl ACID
REFLUX CONDENSER
CW
QUENCH TOWER
CRACKER
FUEL
ETHYLENE DICHLORIDE
STRIPPER
CW
LIGHT ENDS
CW
PRODUCT VINYL CHLORIDE
FRACTIONATOR
HEAVY ENDS PURGE
RECYCLED HEAVIES

PROCESS: DEHYDROCHLORINATION OF ETHYLENE DICHLORIDE

Process: Dehydrochlorination of Ethylene Dichloride

EDC is dehydrochlorinated in a furnace over a mercuric chloride catalyst supported on charcoal. The temperature is 900C and the pressure is 50 pounds per square inch gage. After cooling with liquid EDC in a quenching tower, the HCl is separated from the products of the furnace. In a stripping column, the light ends are stripped from the vinyl chloride. The vinyl chloride is then fractionated, coming off overhead. The heavies are recycled.

The raw materials are EDC and mercuric chloride catalyst. The by-product is hydrogen chloride. The yields are over 95 percent.

There is one source of air pollution, the tail gas scrubber on the hydrogen chloride recovery system.

PR 10P

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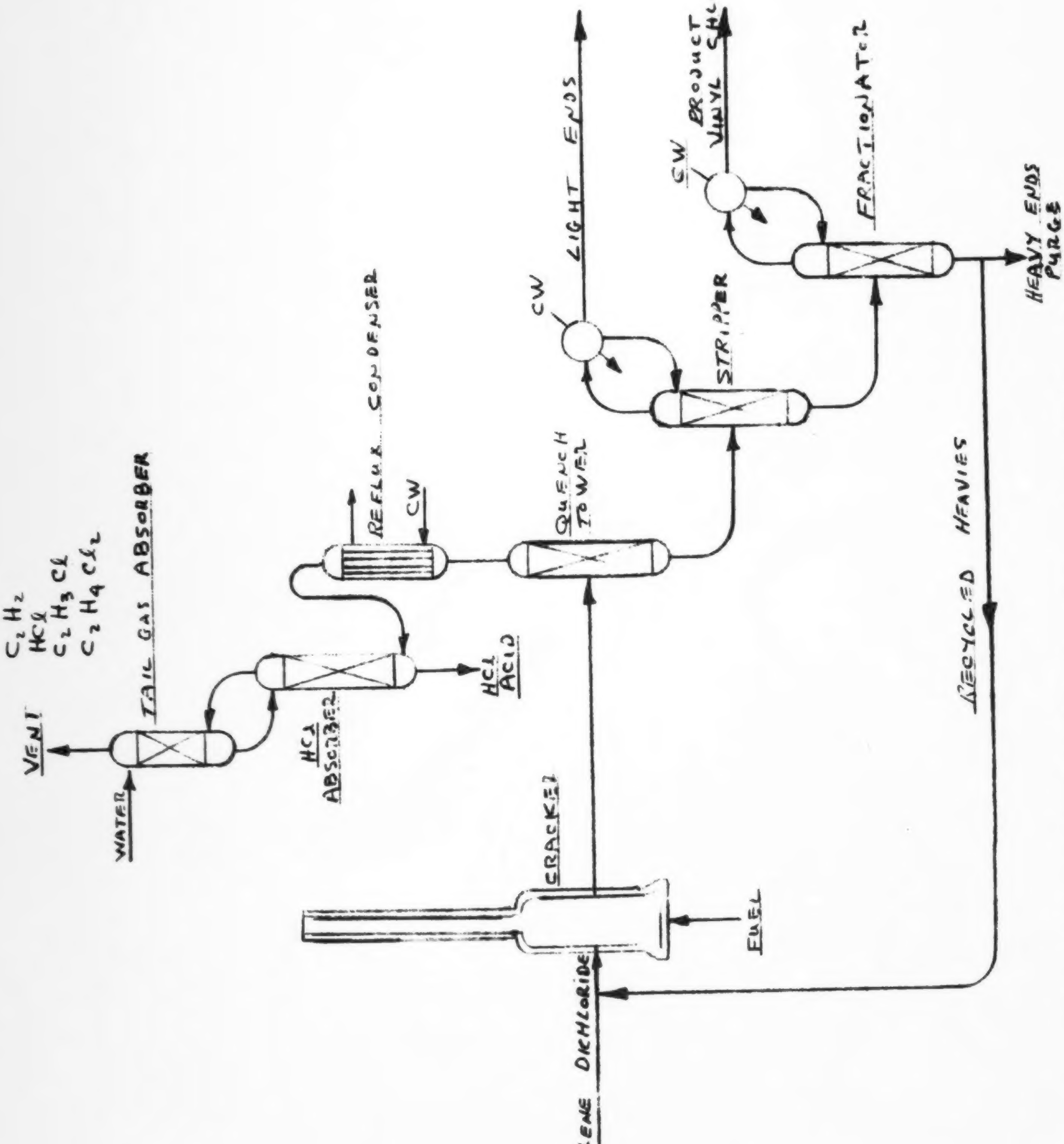
CINCINNATI NEW YORK

Job EPA
Location CHLORINE STUDY
Subject VINYL CHLORIDE

File No. 3383 Sheet No. 1
Checked by ______ Date ______
Computed by JPK Date 11-4-71



ETHYLENE DICHLORIDE
FUEL
CRACKER
QUENCH TOWER
REFLUX CONDENSER
CW
HCl ABSORBER
HCl ACID
TAIL GAS ABSORBER
WATER
VENT
C_2H_2
HCl
C_2H_3Cl
$C_2H_4Cl_2$
STRIPPER
CW
LIGHT ENDS
FRACTIONATOR
CW
PRODUCT VINYL CHLORIDE
HEAVY ENDS PURGE
RECYCLED HEAVIES

PROCESS: DEHYDROCHLORINATION OF ETHYLENE DICHLORIDE

PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO.	INDUSTRY	PRODUCT
2821	PM, SR	VINYL CHLORIDE, C_2H_3Cl

DATE:	PROCESS
11-1-71	DEHYDROCHLORINATION OF 1-2 DICHLOROETHANE

COMPUTER CODE NOS.

SIC. NO. :	COLS. 1-4	☒	2	8	2	1
PRODUCT :	COLS. 5-8	☒		1	3	1
PROCESS :	COLS. 9-13				4	7

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
167	AMERCHEM	WATSON, CA	A	170	B
53	CONOCO	LAKE CHARLES, LA	A	600	B
38	DOW	FREEPORT TX	A	180	B
38	DOW	OYSTER CREEK, TX	A	700	B
53	DOW	PLAQUEMINE, LA	A	340	B
53	ETHYL	BATON ROUGE, LA	A	270	B
38	ETHYL	HOUSTON, TX	A	150	B
69	GOODRICH	CALVERT CITY, KY	A	1000	B
53	PPG	LAKE CHARLES, LA	A	300	B
38	SHELL	HOUSTON, TX	A	750	B

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 49	☒ 50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO. 2821	**INDUSTRY** PM, SR	**PRODUCT** VINYL CHLORIDE C_2H_3Cl	**COMPUTER CODE NOS.**
DATE PREPARED 11-1-71	**PROCESS** DEHYDRO-CHLORINATION OF 1,2-DICHLOROETHANE	**SOURCE** TAIL GAS ABSORBER	

COMPUTER CODE NOS.					
SIC. NO. : COLS. 1-4	☒	2	8	2	1
PRODUCT : COLS. 5-8	☒		1	3	1
PROCESS : COLS. 9-13				4	9
SOURCE : COLS. 14-17	☒			4	1

POLLUTANT / CONTROL DEVICE

DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
HCl	0.2	C	NONE				
C_2H_3Cl	10	C	"				
1,2 $C_2H_4Cl_2$	0.3	C	"				
1,1 $C_2H_4Cl_2$	0.8	C	"				
C_2H_2	3	C	"				

COMPUTER CODE NOS.

PNO 18-20	CNO 21-23	UNCON EMISS 24-30	Q 31	CEF 32-35	Q 36	SCF 37-40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ______

RELATED INDUSTRIES

BIBLIOGRAPHY

Process: Hydrochlorination of Acetylene

The vapor-phase reaction between acetylene and hydrogen chloride in the presence of a mercuric chloride catalyst yields vinyl chloride. Anhydrous hydrogen chloride (slight excess) and dry, purified acetylene gas (free from ammonia, hydrogen sulfide, phosphine, and arsine) are mixed and fed to a reactor containing carbon pellets impregnated with mercuric chloride. The reaction is exothermic, so a coolant is circulated around the tubes to hold the reaction temperature at about 200C and 10 pounds per square inch gage.

Effluent gases from the reactor are cooled by heat exchange and finally condensed and fractionated in a refrigerated column from which unreacted acetylene and hydrogen chloride go overhead. The acid-free monomer or "crude" is further fractionated in a second column in which vinyl chloride goes overhead, and by-product ethylidene chloride and aldehydes are removed as bottoms. The condensed vinyl chloride is stabilized with a small amount of phenol before going to storage. Yields are about 80 to 85 percent.

The raw materials are hydrogen chloride (dry), acetylene, dry (high purity) and mercuric chloride catalyst. The by-products are ethylidene dichloride and aldehydes.

There is a purge on the recycled acetylene to prevent the buildup of inerts, which are mainly impurities in the raw materials.

R 109

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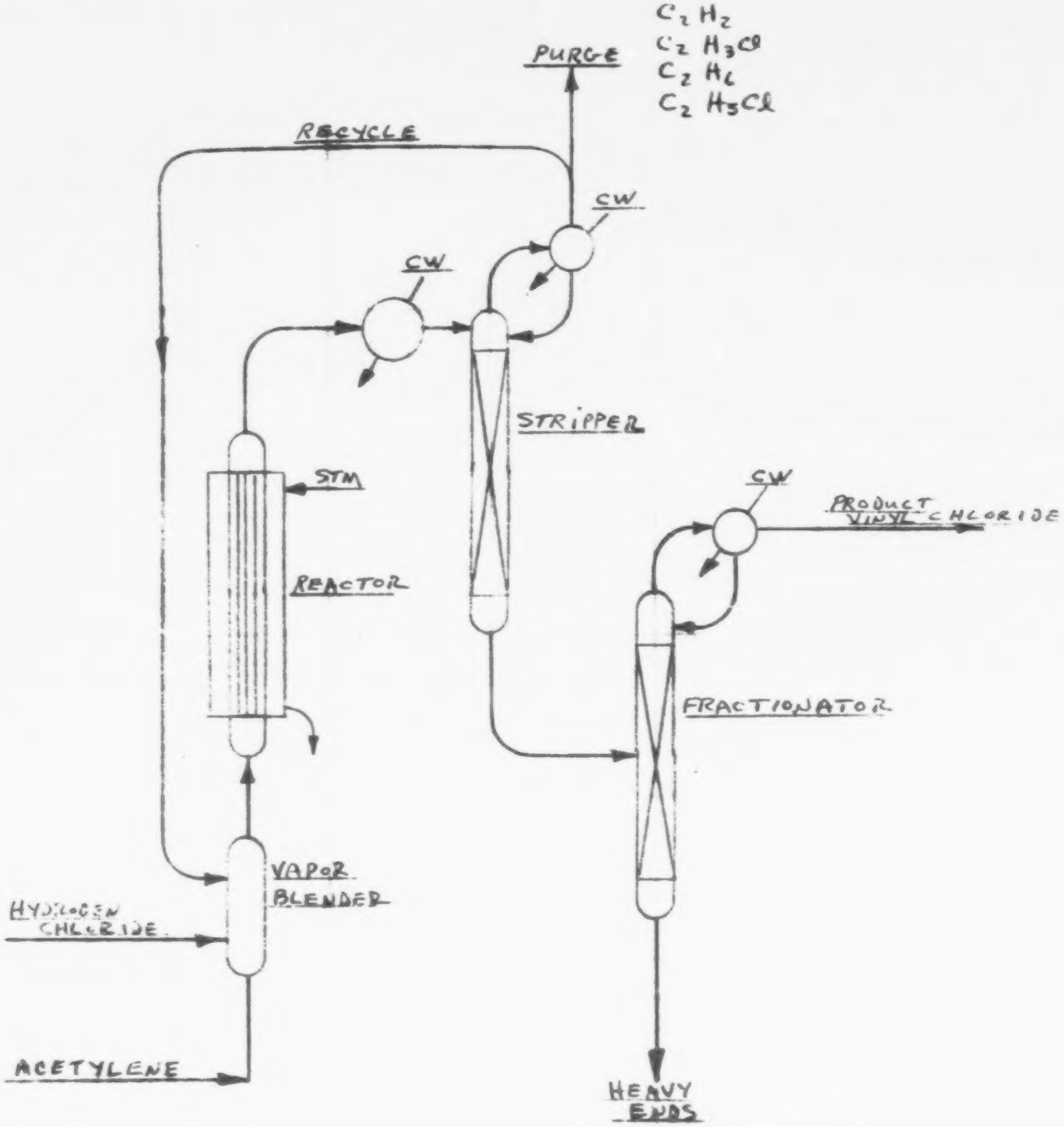
CINCINNATI NEW YORK

Job EPA
Location CHLORINE STUDY
Subject VINYL CHLORIDE

File No. 03383 Sheet No. 1
Checked by ______ Date ______
Computed by SPK Date 11-4-71


PURGE
C_2H_2
C_2H_3Cl
C_2H_6
C_2H_5Cl
RECYCLE
CW
CW
STRIPPER
CW
PRODUCT VINYL CHLORIDE
STM
REACTOR
FRACTIONATOR
VAPOR BLENDER
HYDROGEN CHLORIDE
ACETYLENE
HEAVY ENDS

PROCESS : HYDROCHLORINATION OF ACETYLENE

PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO. 2821	INDUSTRY PM, SR	PRODUCT VINYL CHLORIDE C_2H_3Cl
DATE: 10-27-71	PROCESS HYDROCHLORINATION OF ACETYLENE	

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	☒	2	8	2	1
PRODUCT : COLS. 5-8	☒		1	3	1
PROCESS : COLS. 9-13				4	6

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
53	ALLIED	GEISMAR, LA	A	300	C
53	MONOCHEM	GEISMAR, LA	A	300	C
38	TENNECO	HOUSTON, TX	A	255	C

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 48	50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO. 2821	**INDUSTRY** PM, JR	**PRODUCT** VINYL CHLORIDE, C_2H_3Cl	**COMPUTER CODE NOS.**
DATE PREPARED 10-27-71	**PROCESS** HYDROCHLORINATION OF ACETYLENE	**SOURCE** STRIPPER	

COMPUTER CODE NOS.

SIC. NO. :	COLS. 1-4	☒	2	8	2	1
PRODUCT :	COLS. 5-8	☒		1	3	1
PROCESS :	COLS. 9-13				4	6
SOURCE :	COLS. 14-17	☒			3	6

POLLUTANT / CONTROL DEVICE

DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
C_2H_2	10	C	NONE				
C_2H_3Cl	5	C	"				
C_2H_6	5	C	"				
C_2H_3Cl	12	C	"				

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23	UNCON EMISS 24 30	Q 31	CEF 32 35	Q 36	SCF 37 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING ____________

RELATED INDUSTRIES

BIBLIOGRAPHY

SECTION III - CONCLUSIONS

A. GENERAL

In general, chlorination processes are designed to give high efficiency containment of potentially hazardous emissions of Cl_2, HCl, and chlorinated hydrocarbons within the process. They do not always have control equipment installed exclusively for the purpose of preventing emissions, but typically they will have one or more gas cleaning devices installed to collect unreacted gases and vapors so that they can be recycled to the process. The cost and the obnoxious character of the materials both provide incentives for high efficiency cleaning,over 95 percent,of exit gases.

The collection methods used are condensation, adsorption, and absorption. Condensers and solid adsorbents are generally used to collect materials for recycle to the process. The data available on adsorption are limited, but metal oxides, molecular sieves, silica gel, activated carbon, and alumina have been used. The adsorbent is used to collect and concentrate dilute components in exit gases. Absorption systems are most commonly used for final gas cleaning. Scrubbing liquids used include water, caustic solutions, lime or limestone slurry, carbon tetrachloride, sulfur monochloride, benzene, and toluene. Where high efficiency scrubbing is practiced with organics, absorbent losses will be the main atmospheric pollutant, e.g., where toluene or benzene is used to clean emissions from equipment handling phosgene. Generally, such systems are used, because of the cost,only for very hazardous materials.

It was not possible in the present study to determine whether systems are in practice designed to meet prevailing air pollution control requirements. Calculated emission factors for processes relying exclusively on condensation control suggest that they may not meet the requirements of some agencies, but high levels of control can be effected using sorbent systems so that prevention of air pollution from routine operations does not appear to be dependent upon availability of improved technology.

Consideration was given to the potential for production of hazardous emissions when processes are out of control. All of the processes studied are exothermic, but most seem unlikely to be prone to run out of control so that it will become necessary to open the reactor to the atmosphere to prevent a disaster. Many are liquid phase reactions and consequently are not subject to violent upsets. For the gas phase reactions, large excesses of one reactant will generally be used. While this approach gives potential for loss of control if a massive increase in minor reactant feed were to occur, control system designs make this unlikely in practice for most processes studied. The reaction of H_2 and Cl_2 to produce HCl is one exception which was noted, and others could exist. It does not appear, however, that this problem is of sufficient magnitude to warrant special consideration in a Federal R&D program, but further investigation of industry practice may be desirable to confirm conclusion which is based on limited data.

At present, no feedback control system can be designed to respond to Cl_2 and/or HCl in exit gas streams because of the unavailability of methods of analysis for Cl_2 and HCl. It is conceivable that the availability of a feedback system would permit economies in emissions control and might be useful in preventing some process upsets and attendant emissions to the atmosphere. Definitive estimates of potential impact of successful work to develop a feedback system could not be made but incentives for such work appear to be weak. Lastly, calculated emission factors suggest the need for further study.

B. POLLUTION BY PROCESSES

Totaling the emission factors as shown on the source data tabulation sheets for each process and using the production data of Table 3, the total quantity of air pollutants for each process was calculated for 1970. The results are shown in Table 4.

TABLE 4 - TOTAL EMISSIONS BY CHLORINATION PROCESSES

	Process	Product	Class of Product	Production 10^6 Lbs./Year	Total Emission Factor, Lbs./Ton	Total Pollution 10^6 Lbs./1970
1	Chlorination of Ethylene	$C_2H_4Cl_2$	1	4420	27	59.7
2	Oxyhydrochlorination of Ethylene	$C_2H_4Cl_2$	5	780	106	41.4
3	Chlorhydrination of Propylene, Then Hydrolysis	C_3H_6O	1	1100	59	32.4
4	Chlorination of Propylene	C_3H_5Cl	3	870	54	23.5
5	Dehydrochlorination of DCE	C_2H_3Cl	4	2600	14.3	18.6
6	Hydrochlorination of Acetylene	C_2H_3Cl	2	650	32	10.4
7	Hydrochlorination of Ethylene	C_2H_5Cl	2	512	32	8.2
8	Hydrochlorination of Vinyl Chloride, Then Chlorination	$C_2H_3Cl_3$	2-3	420	38	8.0
9	Chlorination of Benzene	C_6H_5Cl	1	600	24	7.2
10	Chlorination of Methane	CCl_4	3	360	36	6.5
11	Chlorination of Propane	C_2Cl_4	3	620	20	6.2
12	Chlorination of Methane	CH_2Cl_2	3	330	36	5.9
13	Chlorination of Methane	CH_3Cl	3	300	36	5.4
14	Chlorination of Methane	$CHCl_3$	3	250	36	4.5
15	Chlorination of Carbon Disulfide	CCl_4	1	225	34	3.8
16	Chlorhydrination of Allyl Chloride, Then Hydrolysis	C_3H_5OCl	1	590	12	3.5
17	Oxyhydrochlorination of Dichloroethane	C_2HCl_3	5	60	109	3.3
18	Chlorination of Propane	CCl_4	3	315	20	3.2
19	Chlorination of Acetylene, Then Dehydrochlorination	C_2HCl_3	1-4	530	7.2	1.9
20	Hydrochlorination of Ethanol	C_2H_5Cl	2	64	42	1.3
21	Chlorination of Ethane	C_2H_5Cl	3	64	33	1.1
22	Chlorination of Trichloroethylene, Then Dehydrochlorination	C_2Cl_4	1	160	10.9	0.9
23	Chlorination of Carbon Monoxide	$COCl_2$	3	560	2.5	0.7
24	Chlorination of Hydrogen	HCl	3	265	1.1	0.1
25	Hydrochlorination of Methanol	CH_3Cl	2	90	0	0

SECTION IV - RECOMMENDATIONS

It is recommended that consideration be given to field investigation of current practice to define the economic limitations for the best available control technology. This would provide information useful both in setting standards and in the refinement of R&D objectives.

While R&D work, targeted specifically at prevention of emissions from chlorination processes, does not seem to be needed, present and contemplated studies of control devices should consider the possible applicability of development work to produce increased efficiency and lower costs for control.

SECTION V - BIBLIOGRAPHY

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1962	TC Publication	114	TC 1.33:962
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1964	TC Publication	167	TC 1.33:964
1965	TC Publication	206	TC 1.33:965
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